

# FLOTATION

BY . . .

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• TO

ARTHUR FAY TAGGART

*in appreciation of the services he has rendered  
to the metallurgical profession  
and in grateful acknowledgment of the inspiring teaching  
which it was my good fortune to receive from him*



## PREFACE

Twenty-five years ago the possibility of concentrating ores by flotation was regarded as remote, if indeed that process was at all considered. Today it is universally practiced, and its field of application is being extended daily. The span of a quarter of a century has seen the patenting of varied flotation processes and machines, but a good deal of standardization has taken place, as the best were recognized.

A growing interest in the process and its application is manifest, not only among those engaged in the mining and metallurgical profession and among students, but also among laymen who wish to invest in mining enterprises involving flotation operations and among chemists who see in the process a field of endeavor worthy of their best efforts.

In writing this book it has been my aim to prepare a manual that would serve as an introduction to the subject, for metallurgists, chemists, college students, and business men. The book is, therefore, largely a technological record of the art, built on a scientific foundation and framed by its economic background. Chapter I is historical; Chapters II to IV present the fundamental chemistry; Chapters V to VII, XIV, XV, XVIII, and XIX the general technology; Chapters VIII to XIII the detailed technology and practice; and Chapters XVI, XVII, and XX the economics of the art. These, however, are not hard-and-fast divisions, and there is much overlapping of the principal objectives.

It has been said that the great difficulty in preparing a book is to know what to leave out. This I have found to be very true. After much debate, I decided to omit descriptions and discussion of the crushing and grinding phases of the art (except in an incidental manner) and, likewise, to minimize the space devoted to flotation machinery and to mill design. The subject of crushing and grinding is so vast that its inclusion in this book would have reduced the space available for discussion of flotation proper; data on machinery can be had readily from the manufacturers; design is a vast subject about which detailed informa-

tion is not needed by the average reader for whom this book is written.

\* The historical and legal phases of the process are treated in an incidental manner only. This has been done not to minimize the contributions of those who developed the art, but out of regard for the reader who may construe such details as of academic interest only. Also, the patent situation has shown signs of getting straightened out: the ominous suits of fifteen years ago are fortunately largely settled.

The preparation of this book would have been impossible without the generous cooperation of a great many technicians.

First of all, I wish to record my obligation to those who have contributed their knowledge to the technical press. To these sometimes unseen or anonymous collaborators my thanks are due. I have tried to acknowledge my obligation by reference. No doubt I have failed in many places, but I hope these oversights will be condoned.

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# CONTENTS

	PAGE
PREFACE. . . . .	vii
INTRODUCTION BY THEODORE J. HOOVER . . . . .	xv
CHAPTER I	
HISTORICAL SURVEY OF FLOTATION . . . . .	1
CHAPTER II	
THE PHYSICOCHEMICAL FOUNDATIONS OF FLOTATION . . . . .	9
Properties of Matter in Bulk—Surface Reactions	
CHAPTER III	
THE PHASES IN FLOTATION SYSTEMS . . . . .	24
The Gaseous Phase—The Liquid Phase—The Solid Phases	
CHAPTER IV	
COLLOID SYSTEMS. . . . .	40
CHAPTER V	
FLOTATION REAGENTS . . . . .	54
Frothing Agents—Collecting Agents—Organic Inhibitors—Inorganic Non-frothing Non-collecting Agents—Use of Reagents	
CHAPTER VI	
MECHANICAL ASPECTS OF FROTH PRODUCTION . . . . .	86
Gas Introduction—Methods of Gas-solid Attachment—Structure and Size of Mineralized Bubbles—Froth Formation—Froth Characteristics—Froth Characteristics Desired by the Operator	
CHAPTER VII	
LIBERATION AND PARTICLE SIZE . . . . .	120
Ore Texture—Effect of Ore Genesis—Liberation—Particle Size and Floatability	
CHAPTER VIII	
FLOTATION OF SULFIDE ORES OF COPPER . . . . .	156
The Problems Involved—Specific Behavior of Various Minerals—Reagent Consumption—Practice	

	PAGE
CHAPTER IX	
THE FLOTATION OF SULFIDE LEAD-ZINC ORES . . . . .	196
Flotation of Pure Minerals—The Problems in the Treatment of Lead-zinc Ores—Reagent Consumption—Practice . . . . .	.
CHAPTER X	
SULFIDE COPPER-ZINC, COPPER-LEAD, AND COPPER-NICKEL ORES . . . . .	248
Copper-zinc Ores—Copper-lead Ores—Copper-nickel Ores . . . . .	.
CHAPTER XI	
OXIDIZED ORES OF COPPER, LEAD, AND ZINC . . . . .	290
Lead-silver Ores—Copper Ores—Zinc Ores—Selective Flotation of Mixed Base-metal Carbonate Ores . . . . .	.
CHAPTER XII	
PRECIOUS AND RARE METALS . . . . .	320
Gold and Silver—Platinum Ores—Mercury Ores—Molybdenite Ores . . . . .	.
CHAPTER XIII	
NON-METALLIC MINERALS . . . . .	343
Non-polar Non-metallic Minerals—Coal—Polar Non-metallic Minerals . . . . .	.
CHAPTER XIV	
MACHINERY . . . . .	387
Flotation Machines—Auxiliary Machinery . . . . .	.
CHAPTER XV	
SOME POINTERS ON MILL DESIGN . . . . .	411
Plant Capacity—Location—Water Supply—Tailing Disposal—Mill Arrangement . . . . .	.
CHAPTER XVI	
ELEMENTS OF COSTS . . . . .	433
Overhead Costs—Capital or First Cost—Operating Costs . . . . .	.
CHAPTER XVII	
CHOICE OF ORE-TREATMENT METHOD . . . . .	457
Smelter Schedules—Choice between Floating before Smelting and Direct Smelting—Custom Flotation Plants—Choice between Flotation and Leaching—Treatment of Precious-metal Ores— Choice between Flotation and Gravity Concentration—Choice between Several Flotation Alternatives . . . . .	.



## CONTENTS

xiii

PAGE

### CHAPTER XVIII

TESTING AND TESTING EQUIPMENT . . . . .	488
---	-----

Batch Testing—Translation of Batch Testing to Plant Operation—  
Microscope Laboratory Equipment and Its Use—Chemical Equip-  
ment and Laboratory—Crushing, Grinding, and Sizing Equipment  
and Testing—Flotation Equipment and Its Use—Arrangement  
of Equipment—Keeping Records of Flotation Tests

### CHAPTER XIX

METALLURGICAL CALCULATIONS. . . . .	522
-------------------------------------	-----

### CHAPTER XX

EFFECT OF FLOTATION ON MINING, METALLURGY, AND METAL MARKETS . . . . .	531
---	-----

INDEX. . . . .	537
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## INTRODUCTION

That worthy historian Herodotus in the book, *Melpomene*, Chapter 195, describing the country of the Gyzantians, where the men paint themselves red, says there is an island in a lake from which the young maidens of the country draw up gold dust by dipping birds' feathers, smeared with pitch, into the mud. He says: "If this be true, I know not; I but write what is said." He then goes on to describe a method which he had practiced himself for the recovery of bitumen, which was without doubt based on the adhesive factors involved in the processes of flotation in this day; and he draws the inference from his own experience that the story of the maidens is probably true.

The germs of many of the most valuable of the processes and methods of applied science and art of the day have lain long fallow in the records of the past. They are sometimes resurrected and often reinvented. The theory of electricity was elucidated to fullness by Faraday and the main mathematical principles of surface tension were set out by Laplace a century before any extended use. One may well wonder how many more instances of neglected opportunity are in the textbooks and encyclopaedias.

These instances drive home with great force the futilities of the method of empiric invention in this age where there is often complete disregard of the scientific principles involved. There is no doubt that a procedure in which scientific research comes first and invention follows is the most economical both in money and in human effort. Unfortunately, this is not likely to become the sole method of the human race but, as the years go by, there is more and more approach to the scientific method. The vagaries of the patent situation will be somewhat simplified in time by this scientific procedure and there will, in time, be less numerous instances of the law of the land being in direct opposition to the laws of nature.

One of the outstanding merits of this book is that it much more fully than any previous attempt gives a practically complete exposition of the scientific principles underlying a process which is treating millions of tons of ore every year.

THEODORE J. HOOVER.



# FLOTATION

## CHAPTER I

### HISTORICAL SURVEY OF FLOTATION

**Flotation**<sup>1</sup> is a process of ore *concentration*, that is, a method for segregating the minerals in an ore into several products. One of the products of concentration, known as the *tailing*, is made to contain the worthless substances and is discarded; the other products are known as *concentrates* because they contain the valuable substances in the ore in a more concentrated state. Concentrates are treated further by various metallurgical processes such as leaching or smelting.

In order to concentrate an ore it is necessary, first, to crush it so that each particle is composed as nearly as possible of valuable or worthless material only. This step is generally called *liberation*; together with concentration and auxiliary operations such as unloading the ore, conveying, sampling, thickening and filtering of ground ore pulps, loading concentrates, and discarding the tailing, it covers the scope of *ore dressing*.

In flotation the separation of minerals takes place in water in which the solid particles are suspended, and results from the adhesion of some species of solids to gas bubbles which are generated or introduced in the pulp, and the simultaneous adhesion of other species of solids to the water in which they are suspended. Flotation of the solids adhering to the bubbles permits their removal from the pulp as a froth of different composition than the pulp.

Formerly the term *flotation* with descriptive adjectives was used for all processes of concentration in which levitation in water of particles heavier than water was obtained. Thus, if some particles were retained in an oil layer or at the interface between

<sup>1</sup> The term *flotation* is said to be derived from the French *flottaison*. It is rather unfortunate that flotation is not spelled floatation, for the user is faced with the dilemma of choosing between "*floatability*" and "*flotability*" to describe the ability to float.

an oil layer and a water layer, the process was spoken of as *bulk-oil flotation*; if the particles were retained at a free water surface as a layer one particle deep, the process was *skin flotation*; and if the particles were retained as a foamy layer several inches thick, the process was *froth flotation*. Froth flotation is the only process that has survived the test of time, and the term flotation is now used universally to describe froth flotation.

**Early Attempts.**—The earliest known<sup>1,2</sup> recognition of the difference in wettability of minerals by water is recorded in British Patent 488/1860 to William Haynes. Haynes' invention consisted in first triturating dry-ground ore with one-fifth to one-ninth as much fatty or oily agent and then agitating and triturating this mass with water, whereby the combined sulfides and fatty or oily agent were segregated from the combined earthy matter and water. United States Patent No. 348,157/1885 to Carrie J. Everson describes a very similar operation from which, however, improved results were obtained by modifying the water with acids, with acid salts, or with neutral salts. Everson's and subsequent patents, up to Delprat's U. S. Patent 735,071/1903, involved buoyancy of the oil and selection by oil of certain minerals from an acidulated pulp as the cardinal thoughts; this was the era of bulk-oil flotation typified by the Elmore bulk-oil process<sup>(4a)</sup>.

At the other extreme from the processes making use of large quantities of oil to separate particles that are well wetted by water from particles that are wetted less may be placed those generally known as skin-flotation processes, in which dry or drying mineral particles are approached by a free water surface which exerts a selection between the two classes of ore par-

<sup>1</sup> Cornelio L. Sagui<sup>(3)</sup> states that the ancient Greeks used skin flotation in recovering the metallic particles in their crushed ores. It is not known whether Mr. Sagui's interpretation of the ancient texts is metallurgically justified. Thus, the plant he describes could have been used as a stationary table for gravity concentration, the upper part of the mineralized water sheet being rejected and the sediment cleaned by a second operation. If thorough metallurgical study were to confirm Sagui's statement of the use of flotation over 2000 years ago, we would have another proof of the old adage that "there is nothing new under the sun."

According to T. A. Rickard<sup>(2)</sup>, Herodotus reported that gold was recovered from the mud of a lake by means of feathers daubed with pitch and held in the hands of apocryphal virgins.

<sup>2</sup> Superior **bold-face** figures in parentheses indicate references to Literature Cited at end of chapters.

ticles<sup>(6)</sup>. Typical apparatus was described by Nibelius (U. S. Patent 486,495/1892), Macquisten (U. S. Patents 865,194-5/-1907), DeBavay (U. S. Patent 864,597/1907), and Wood (U. S. Patent 1,088,050/1914).

**Gas as Buoyant Medium.**—The period from 1901 to 1905 is marked by the Australian invention of flotation processes *in which the buoyant medium is a gas*. Guillaume Daniel Delprat (U. S. Patent 735,071/1903 and British Patent 26,279/1902) and Charles Vincent Potter (U. S. Patent 776,145/1904) obviously used as buoyant medium the gas produced by the reaction of a strongly acid pulp (pH 0-3) with suspended sulfides and carbonates; recognition of this important principle is found in British Patent 12,778/1902 to Alcide Froment. Quoting from Hoover<sup>(1a)</sup>:

He [Froment] says that the oiled mineral particles collected in spherules and were carried to the surface by gas bubbles. Finally he enunciates this important principle: "The rapidity of the formation of the spherules and their ascension is in direct ratio to the quantity of gas produced in the pulp in a given time."

The production of gas bubbles by chemical reaction between the pulp and suspended solids and flotation of sulfides thereby has been called flotation by chemical generation<sup>(4b)</sup><sup>1</sup>. It is typified by the Potter-Delprat process. Production of a gas by electrolysis of water was suggested by Francis Edward Elmore (British Patent 13,578/1904) but it was not applied industrially. The vacuum generation of gas bubbles (British Patent 17,816/1904), also invented by Elmore, was a definite industrial success and could, no doubt, be used today<sup>(1b)</sup>.

*Direct introduction of gas* by a beater or impeller revolving in a pulp is featured in U. S. Patent 835,120/1906 to Sulman, Picard, and Ballot and, more especially, in U. S. Patent 953,746/1910 to Theodore J. Hoover. Figure 1 is a drawing of the Hoover apparatus; in it may be recognized the essential features of flotation machines of the *agitation* type of today. Direct introduction of gas through a porous bottom (Callow, U. S. Patent 1,104,755/1914) and from submerged pipes (Forrester and Hunt cells) are later developments in the methods of gas introduction.

**Reduction in Amount of Oil.**—With the replacement of a gas for oil as the buoyant medium came, first, the recognition that

<sup>1</sup> Chap. VI, p. 86.

the use of large amounts of oil is unnecessary; and, later, the discovery that it is definitely objectionable. United States Patent 835,120 marks the first step in the reduction in the amount of oil used, the interpretation of the Courts concerning this patent being, indeed, that its application is limited to the use of less than one per cent of oil (reckoned with reference to the weight of ore treated). Universal modern usage, in quantifying the

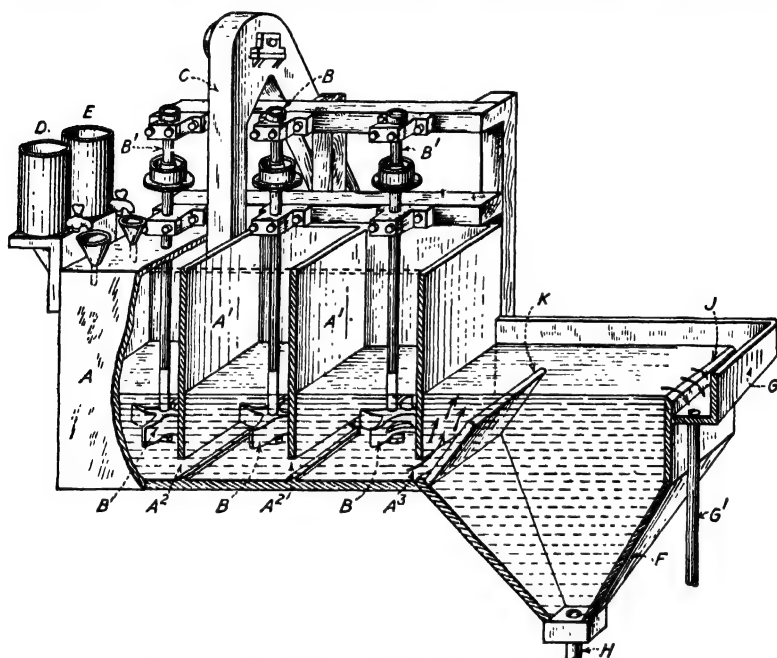


FIG. 1.—Hoover Flotation Machine. (After Hoover.)

reagents used in flotation, is to express the amount of reagent in pounds per ton of ore (lb. per ton); thus one per cent of oil is the equivalent of 20 lb. of oil per ton of ore (20 lb. per ton). In those plants in which oil is still used in an amount sufficient to exceed saturation of the water with dissolved oil, the amount of oil ranges from 0.3 to 2.0 lb. per ton, which is but a mere fraction of what was used in the early days.

As the desirability of reducing the amount of oil used gained acceptance, it became recognized that oily substances are not all alike in flotative properties. The first step in this direction was taken by Greenway, Sulman, and Higgins (U. S. Patent 962,678/1909), who recommended the use of soluble *frothing*





to be one of the most useful in the art of flotation. In 1912 Lowry and Greenway discovered that dichromates inhibit galena (Australian Patent 5,065/1912).

Alkaline circuits were introduced from about 1921 and have become standard practice in the flotation of sulfide ores because of their great advantage over acid circuits. Incidentally they led to the discovery of the marked inhibiting property of lime for pyrite and have made possible the use of effective selective agents such as sulfites (Pallanch, U. S. Patent 1,486,297/1924), cyanides (Sheridan and Griswold, U. S. Patents 1,421,585/1922, 1,427,235/1922) and sulfides (Hellstrand, U. S. Patent 1,469,042/1923). These selective agents permit the flotation of one mineral but inhibit that of another, so that a separation may be obtained. Flotation using selective agents has been termed *selective flotation*, as contrasted with *collective flotation* in which all metals are collected in one concentrate; it has also been termed *differential flotation*. It would seem as though there is no need for a qualifying adjective since all flotation operations are selective as between sulfides and gangue—or as between one sulfide and another. In this book the unqualified noun is used throughout, except where it is desired to bring out a contrast to collective flotation.

Table 1 summarizes the important steps in the evolution of flotation from crude beginnings to a fool-proof, elaborate, and scientifically amazing application of chemistry to ore concentration.

**Recent Trends.**—Flotation has satisfactorily solved the treatment of complex lead-zinc-iron and copper-iron sulfide ores; in the treatment of ores of this kind, future developments will center largely around an improvement in recovery of metal in the very coarse and extremely fine particles, and of selection among the finer particles. The treatment of sulfide copper-zinc ores and sulfide copper-lead ores is only partially solved. In this direction, as in the treatment of lead-zinc and copper-iron sulfide ores, the discovery of more selective collectors than are available at present will perhaps lead to an improved technical performance.

Relatively speaking, the application of flotation to oxidized ores has been disappointing, although a few instances of success—at high reagent cost—can be pointed out. Progress in this direction, as well as in the flotation of oxide, carbonate, sulfate, and silicate ores of metals other than the noble metals and lead,

TABLE 1.—IMPORTANT STEPS IN THE EVOLUTION OF FLOTATION

Approximate date	Name of inventor	Invention
1860	Haynes	Usefulness of differences in wettability of minerals by water and oil.
1886	Everson	Acidulated pulps desirable.
1902	Froment; Potter, and Delprat	Gas as a buoyant medium.
1905	Schwarz	Sodium sulfide to recover oxidized base-metal minerals.
1906	Sulman, Picard, and Ballot	Reduced amount of oil; introduction of gas by violent agitation.
1909	Greenway, Sulman, and Higgins	Soluble frothing agent.
1913	Bradford	Copper sulfate as activator for sphalerite.
1913	Bradford	Sulfur dioxide to depress sphalerite.
1921	Perkins	Specific organic collectors.
1921	.....	Alkaline circuits.
1922	Sheridan and Griswold	Cyanides to depress sphalerite and pyrite.
	Keller	Xanthate.
	.....	Soaps for flotation of non-metallics.

copper and zinc, should mark the next decade of development of the flotation process.

The complexity of the physicochemical phenomena that play a part in flotation is probably unequalled in any other metallurgical field; in this respect, flotation more nearly approaches the chemical processes dealing with matter in a fine state of division, as the ceramic, leather, or food industries. In order to make it possible to grasp the full play of the physicochemical forces of flotation it has seemed desirable to discuss in the following chapters, at some length, the physicochemical phenomena displayed by surfaces.

4. TAGGART, A. F.: "Handbook of Ore Dressing," a, pp. 787-790; b, 790-793, John Wiley & Sons, Inc., New York, .
5. WAINWRIGHT, W. E.: "The development of processes for the treatment of crude ore, accumulated dumps of tailing and slime at Broken Hill, New South Wales," Third Empire Mining and Metallurgical Congress, South Africa (1930).
6. WOOD, HENRY E.: "Early efforts in flotation of dry minerals," *Eng. Mining Jour.*, **126**, 571-573 (1928). .

## CHAPTER II

### THE PHYSICOCHEMICAL FOUNDATIONS OF FLOTATION

The marked effect of extremely small amounts of some reagents added to flotation systems has caused flotation to be looked upon as a process based on the behavior of surfaces, and has led investigators to seek a relation between the properties of the surfaces of solids and liquids, considered in the light of their atomic structure, and the flotative properties of solids in aqueous pulps. This search has been fruitful in building up a theoretical foundation for flotation phenomena, as well as in blazing the trail for further improvements in technique. In order to present clearly the modern flotation theory, it will be necessary to review some of the most important concepts of physical chemistry that concern the structure of matter.

#### PROPERTIES OF MATTER IN BULK

**Atoms and Molecules.**—It is generally conceded that matter is atomic in structure, meaning that it cannot be subdivided in the ordinary sense of the word, except as integral multiples of certain discrete particles known as *atoms*. These atoms are more or less loosely grouped together as *molecules*. A *gram-atom* of any substance, whose weight in grams equals the atomic weight of that substance, contains the same number of atoms, in round numbers 606,200,000,000,000,000,000,000. The gram-molecule or *mol* is similarly defined as that quantity of a certain substance which contains  $6.062 \times 10^{23}$  molecules. The number  $6.062 \times 10^{23}$  is known as the Avogadro number. By its use, knowing the specific gravity and atomic weight of an element, it is possible to determine the volume of space occupied by each atom.

Thus, an atom of solid lead occupies  $\frac{207}{11.7 \times 6.06 \times 10^{23}}$  or  $2.92 \times 10^{-23}$  c.c., which is equivalent to the space occupied by a cube having an edge of  $3.1 \times 10^{-8}$  cm., a very small volume, indeed. Because of the minuteness of molecular and atomic dimensions when expressed in centimeters or inches, a new unit,

known as the *Ångström* ( $\text{\AA}$ ) has been introduced. The *Ångström* is equal to one ten-millionth part of a millimeter. The volume of space occupied by a lead atom, for instance, is  $29.2\text{\AA}^3$ .

**The Structure of Atoms.**—Just as the work of physicists of the nineteenth century led to the conclusion that matter is composed of atoms, so that of physicists of the present century has brought to light considerable data as to the structure of atoms. The interpretations from these data, although frequently contradictory in detail, agree well in most important respects. Thus, all of the evidence points to a dual structure of atoms, one part being associated with a positive charge of electricity and generally known as the *nucleus*, and the other being composed of one or several identical charges of negative electricity known as *electrons*, whose mass is much smaller than that of the nucleus and apparently entirely due to their charge and velocity.

A number of attempts have been made to construct models of atoms that would be concrete enough to be understood, and at the same time mathematically possible and in agreement with the observed facts. The most successful attempts have been those of Bohr<sup>(6)</sup>. Although Bohr's original model of the hydrogen atom, or the more recently introduced abstract mathematical models based on the conceptions of wave mechanics<sup>(2)(21)(10)</sup> have satisfied the physicists, no atomic conception seems to explain ordinary chemical reactions better than the well-known Lewis-Langmuir model<sup>(15)(11)</sup>.

Working independently, Lewis and Langmuir arrived at the conclusion that atoms must consist of a nuclear positive charge equivalent to the sum of the charges on all the electrons, and that these electrons are arranged at fixed positions in concentric shells incapable of containing more than a definite number of them. The maximum electron content of the innermost shell is two and that of each subsequent shell is eight, hence the name of "octet theory," which has been applied to the Lewis-Langmuir conception. It should be noted, by the way, that this theory does not differ from that of Bohr except in that the electrons are supposed to occupy fixed positions instead of revolving in definite orbits. The octet theory postulates that the electrons always arrange themselves so as to complete the inner shells before the outer shells are occupied (although there are exceptions among atoms of more complex structure, such as the *rare earths*). According to the octet theory, as well as according to Bohr and

to others, there is a considerable space void of *matter* between the nucleus and the electrons.

**The Periodic Table.**—The explanation of chemical behavior which is offered by the Lewis-Langmuir octet theory is related to the periodic table or periodic arrangement of the elements (Table 2). According to Lewis and Langmuir, chemical reaction is a manifestation of the tendency on the part of atomic nuclei to acquire from, give up to, or pool electrons with other nuclei. The atoms of the elements which have a complete shell of electrons are electrostatically neutral. Also, they are in the structure of highest symmetry and, therefore, of least potential energy; consequently, they have no tendency to react with other atoms or among themselves. These elements constitute the noble gases such as argon, neon, and helium; they occur as monatomic molecules. The elements that lack just one electron to complete their outer shell (or shell of "valence electrons") and those which have one electron in the valence shell are among the most active of the elements: they constitute the halogens and the alkali metals. Alkali metals and halogens possess particular affinity for each other, due, no doubt, to their being able to satisfy mutual needs. Their union is exothermic and yields stable salts. The reaction of the metals which have two electrons in their outer shell with the non-metals which lack two electrons, as the reaction of calcium with oxygen, is exothermic although less violent than the reaction between sodium and chlorine, for instance. In the same way, the reaction between aluminum and arsenic, or between carbon and silicon, are respectively increasingly difficult to bring about.

**Ions and Polarity.**—Salts, as of alkalis with halogens, in the fused state or when dissolved in certain solvents, conduct electricity; this is explained by considering the salts as ionized, that is by looking upon their molecules as broken up into *ions* possessing an electric charge and therefore moving in the fluid under the potential difference existing between the electrodes, and thus carrying the current in the electrolyte. Because of the non-reactive character of their electronic configuration these ions present little tendency to adhere to each other, and yet they cannot be separated by any great distances except upon expenditure of very considerable energy.

Substances such as the salts of the alkali metals with the halogens are ionized, not only in the liquid or dissolved state in





which their ionization is easily displayed by electrolysis, but also in the solid state, as can be shown by *x*-ray analysis. Thus, common salt (sodium chloride) crystals do not consist of molecules of sodium chloride, nor of atoms of chlorine and atoms of sodium, but of sodium and chloride ions arranged in a regular pattern or lattice in such a way that no two ions of opposite character can be singled out as belonging to each other. If this lattice could be magnified sufficiently to be perceived easily, and we were to travel across the crystal in certain directions, positive and negative ions would be encountered alternately. In other words, *poles of electricity* of opposite charge alternate: the substance is polar. A proper understanding of polarity is essential in connection with flotation because of the fundamental rôle which it plays in controlling the adherence of suspended particles to air bubbles or to water.

Although it is entirely clear that in common salt the sodium atom has lost an electron to a chlorine atom, it is much less certain that an aluminum atom loses three electrons in combining with a nitrogen atom, and it is impossible to tell which of the carbon or the silicon atoms has received the necessary electrons in the formation of carborundum ( $\text{SiC}$ )<sup>(16)</sup>. To take a still more extreme example, the formation of an oxygen molecule from two oxygen atoms cannot have resulted from the loss of two electrons by one of the atoms and their acquisition by the other, because the two atoms are identical: the result of their union must be a symmetrical product. It is more likely that the eight electrons necessary for the valence shell are obtained by the pooling or sharing of a number of electrons, together with some electrons individually retained by each of the two atoms. Thus, in the case of the oxygen molecule, two electrons from each atom are pooled, making four shared electrons in all; each atom, then, can use its remaining four individual electrons and the four shared electrons, or eight in all, making an electronically stable structure. As a matter of fact, molecular compounds like the oxygen molecule are much less reactive than the corresponding atomic elements. The recent achievement of a flame of atomic hydrogen, in which hydrogen atoms supply the heat by combining to form hydrogen molecules<sup>(12)(13)</sup> exemplifies this. The flame obtained in this manner is far hotter than any other artificial source of heat, being capable of producing a temperature of about 5000°C. Just as there is no transfer of electrons in the forma-

tion of oxygen molecules from oxygen atoms, so it cannot be said that there is a transfer of electrons in the formation of a number of compounds such as carborundum or the hydrocarbons. Compounds of that type are known as *non-polar compounds* in contrast to the *polar compounds* of the type of common salt. Non-polar compounds have practically no tendency to ionize, do not conduct electricity, have a low dielectric constant, are much less reactive, and, if they react, are involved in much slower reactions or in reactions which are catalyzed by the formation of intermediate compounds of an additive character<sup>(20)</sup>.

In the solid state, non-polar substances differ materially from polar substances in their structure. Because of their lack of polarity or reactivity, molecules of non-polar substances form crystals composed of molecules loosely attached to each other by *cohesive* or *residual valence* forces rather than through the action of forces of the same intensity as those which bring about chemical combination. Non-polar substances differ therefore from polar substances not only in the liquid state, but also in the solid state, in which they occur as aggregates of molecules rather than as aggregates of ions and in which they do not display electrolytic properties.

Although the contrast between extreme examples of these two types of substances is very clear and unmistakable, there exist substances having intermediate properties. The terms "polar" and "non-polar" should therefore be construed to be relative.

**Heteropolar Substances.**—There exists a very important group of substances, the molecules of which are large enough to permit individual consideration of polarity in the several parts of the molecules. Many of these substances are polar in one part and non-polar in another, *e.g.*, valeric acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OH}$ ), which ionizes in water into hydrogen ions and valerate ions ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^-$ ); valerate ions are composed of a small polar group ( $-\text{COO}^-$ ) and of a comparatively large non-polar radical or group ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$ ). In the liquid state, valeric acid is a poor electrolyte. Its solutions in water are poor electrolytes and it crystallizes in leaflets, the thinnest of which consist of two sheets of molecules, each one molecule thick, arranged so that the polar groups of the two planes of molecules face each other in close proximity, whereas the non-polar groups are on the outside of the leaflets. In a thick crystal, slip takes place between adjoining non-polar planes.

"Polar-non-polar," or *heteropolar*, substances are extremely important in surface reactions, and particularly in flotation phenomena.

## SURFACE REACTIONS

The average chemist is far better acquainted with reactions proceeding in the liquid state or in the gaseous state than with reactions involving the solid state. This is because reactions involving the solid state proceed wholly at the surface of junction (*interface*) of the solid and the adjoining medium; even if not complicated by side reactions or the deposition of reaction products at the interface, they are more difficult to study. It is obvious that effects of different intensity may be obtained through the existence of more or less surface. Such a situation does not exist in reactions proceeding in water or in other liquids in which the reactants are dissolved. Besides the fact that the extent of surfaces controls the rate of reactions involving several phases, it must be noted that they possess peculiar structural properties which cause them to appear unsaturated and therefore to present enhanced reactivity. The subject of chemical reaction at solid surfaces is best approached, perhaps, through a study of properties of liquid surfaces which in many respects are similar to solid surfaces.

**The Surface of Liquids.**—Although the molecules, atoms, or ions at liquid surfaces, or within the body of a liquid, are in constant motion, they may be considered as being at definite positions over an infinitesimally short time, and inquiry can be made into their behavior when at rest. Molecules in the body of the liquid are subjected to the cohesive attraction of their neighbors in all directions, the pull being statistically nullified; molecules at the surface of a liquid, on the other hand, are subjected to a much greater cohesive attraction inward than outward, so that the surface behaves as though tightly compressed by an elastic membrane. The surface of liquids is therefore under a tension which, although small in absolute value, is large when it is considered that it is exerted through a depth not exceeding a very few atomic diameters. This *surface tension*<sup>(24)</sup> varies with the composition of the liquid and decreases in general with increasing temperature until the critical temperature of the liquid is attained, at which it is nil. Polar liquids have a comparatively high

surface tension; non-polar and heteropolar liquids a low surface tension. This is shown by Table 3.

TABLE 3.—SURFACE TENSION OF LIQUIDS

Substance	Temperature, degrees centigrade	Surface tension, dynes per centimeter
Water.....	20	72.8
(Non-polar) Hydrocarbons		
Hexane.....	9	18.5
Octane.....	16	21.3
Molten paraffin.....	50	30.6
Benzene.....	20	28.2
Toluene.....	17	28.0
Xylene.....	21	30.0
(Heteropolar) Alcohols		
Methyl alcohol.....	20	23.0
Ethyl alcohol.....	20	22.0
Iso-butyl alcohol.....	20	22.5
Iso-amyl alcohol.....	20	23.1
(Heteropolar) Phenols		
Phenol.....	54	36.5
o-Cresol.....	40	36.2
Thymol.....	25	33.4
(Heteropolar) Nitrogenous Organic Compounds		
Aniline.....	20	40.3
o-Toluidine.....	20	42.5
Dimethyl aniline.....	20	36.0
Pyridin.....	17	38.4
(Heteropolar) Fatty Acids		
Formic acid.....	40	34.2
Acetic acid.....	20	28.5
Iso-butyric acid.....	20	26.0
Iso-caproic acid.....	20	25.3
Acetone.....	19	23.0
Ether.....	20	16.5

Comparison of the surface tension of heteropolar substances is very suggestive of molecular mechanisms. For instance, in the saturated alcohol series, the surface tension of each member of the series is substantially the same at the same fraction of the critical temperature expressed in the absolute scale of temperature. This has been interpreted by Harkins and his col-

laborators<sup>(9)</sup> to mean that the molecules of alcohols at the surfaces of these liquids are oriented in a certain definite way. Furthermore, since the surface tension of alcohols and hydrocarbons is substantially the same, and since they are identical in structure only in the hydrocarbon part of their molecules, it follows that the surface of these liquids must consist of oriented molecules whose hydrocarbon ends are directed toward the gas phase. Langmuir<sup>(10)</sup> has shown that molecules must orient themselves in a very short time (less than one hundred-millionth part of a second), for they are short-lived at the surface of the liquid, molecular motion causing them to return within the liquid or to evaporate.

The surface energy corresponding to surface tension is a form of potential energy; this potential energy tends to be a minimum, in accordance with the second law of thermodynamics which may be stated as follows<sup>(23)</sup>:

"Spontaneously occurring processes are all accompanied by a decrease in the free energy (potential energy) of the system."

The orientation of heteropolar molecules or ions at the surface of a pure liquid may then be looked upon as a result of the tendency for the surface energy to be as small as possible.

**Adsorption.**—Solutions of two liquids in each other are found to have surface tensions that differ from the sum of the surface tensions of proportionate fractions, which one might otherwise be led to expect. This is because the molecules of solvent and solute distribute themselves with a greater proportion, at the surface, of the molecules or ions having the least surface energy. This distribution is in accordance with a famous theoretical equation first derived by Gibbs,<sup>(8)</sup> which is generally formulated as follows:

$$a = - \frac{c}{R\theta} \cdot \frac{\partial T}{\partial c},$$

in which

$R$  = gas constant, in ergs per degree centigrade =  $8.32 \times 10^7$ .

$\theta$  = absolute temperature, in degrees Kelvin.

$c$  = concentration, in any convenient unit, as percentage or gram-molecules per liter.

$T$  = surface tension, in dynes per centimeter.

The quantity  $a$  in Gibbs' equation is called the *adsorption* of the dissolved substance and may be a positive or negative quantity (expressed in gram-molecules per square centimeter of surface).

Langmuir has shown<sup>(11)</sup> that Gibbs' equation leads to the conclusion that the adsorbed layer is one molecule of ion thick.

Gibbs' equation and Langmuir's concrete picture give us a good idea of the local characteristics of dilute aqueous solutions. Thus, we know that dilute solutions of sodium chloride are almost completely ionized; hence a salt solution that is sufficiently weak consists of sodium ions, chloride ions, and water molecules (hydrogen and hydroxyl ions are also present in minor amount); these constituents are distributed at any given instant in random fashion throughout the liquid except at the surface, where there are proportionally more water molecules and fewer sodium and chloride ions down to a depth approximately equivalent to the diameter of a water molecule. In the same way, in a dilute solution of ethyl alcohol in water, the surface contains proportionally many times more alcohol molecules than the bulk of the water; in dilute solutions of a higher alcohol, such as nonyl alcohol ( $C_9H_{19}OH$ ), most of the molecules of alcohol are at the surface and very few in the water; and in the case of still less soluble alcohols and fatty acids, such as cetyl alcohol or stearic acid, substantially all of the solute molecules are at the surface.

**Monomolecular Films.**—Substances insoluble in water, but possessing a polar and a non-polar part in their molecules spread at its surface until they form monomolecular films<sup>(11)</sup>. These films were shown by Adam<sup>(1)</sup> to be either of the solid (or rigid) type, or of the liquid or the gaseous type. The prediction that relations similar to the critical properties of fluids and the equations of state for gases would be experimentally obtained with thin films has been entirely vindicated, and the various investigators engaged in the fascinating study of the behavior of thin films have all observed that a great change occurs in surface forces after the packing of the adsorbed molecules exceeds that at which the molecules can sprawl at will upon the surface. After a complete, closely packed monomolecular layer has been obtained, further additions of the adsorbed substance leads to no substantial change in surface energy, the additional molecules appearing as a jumbled heap on top of the structurally regular monomolecular film. The relation between the surface tension of water and additions of oleic acid is as shown in Fig. 2. Up to additions corresponding to *B* an incomplete monomolecular film of oleic acid is formed at the surface of the liquid. The drop in surface tension that follows further increases in oleic acid to a

quantity corresponding to *C* is caused by crowding of molecules. Further additions of oleic acid beyond that corresponding to *C* cause little further drop in surface tension.

To sum up, it may be said that the properties of a liquid, as viewed from outside the liquid, are those of the outermost layer in the liquid; that this layer which has a depth of a very few molecules is generally different in composition from the bulk of

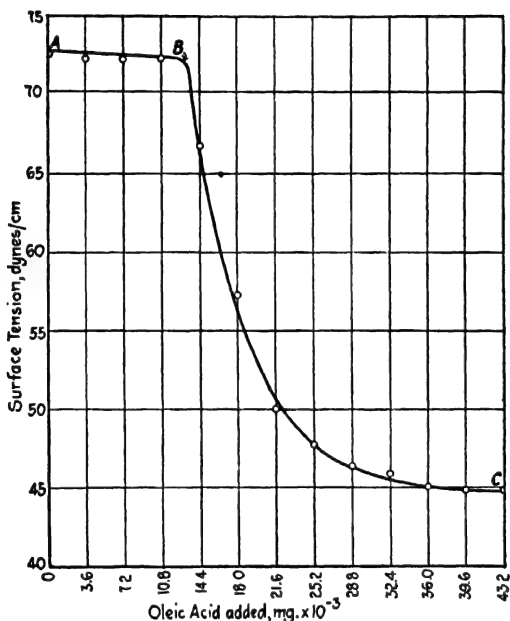


FIG. 2.—Surface tension-concentration curve for oleic acid films on water. Area tested, 135 sq. cm.

the liquid, and that it possesses a definite structure, in contrast with the disorder or random distribution that prevails in the bulk of the liquid.

What has been said concerning the structure of the surface of a liquid holds in substance for the interface between two liquids, with the difference, however, that the properties of the *two* liquids must be considered. Here again, oriented molecules at the interface play a preponderant rôle in determining the structure of the system.

**The Surface of Solids.**—Solid surfaces are similar to liquid surfaces in many respects, although they are rigid instead of

mobile. They are capable of retaining at their surface molecules or ions and they have a definite surface energy which, however, is not directly measurable. Through the retention of adsorbed molecules, atoms, or ions, solid surfaces can bring about a number of reactions which otherwise would not occur between these molecules, atoms, or ions, or which would occur so slowly as to be practically inexistent. Such reactions are said to be *catalyzed* by the surface of the solid which is called a *catalyst*.

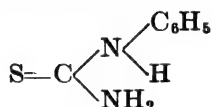
Before dealing further with the properties of solid surfaces, it is desirable to stress the great difference in freedom which exists between the constituent particles of solids and those of liquids: liquids are characterized by disorder in the distribution of their constituent particles except at the surface, where more or less orderly oriented films exist; solids are crystalline, that is, they are characterized by order in the distribution of their constituent particles in the body of the solid and nearly complete order at its surface. Such substances as glass, which are generally termed "solid" because of their rigidity, should rather be looked upon as colloidal dispersions of high viscosity, as super-cooled liquids, or as an additional state of matter, the glassy state<sup>(4)(17)(18)</sup>. According to modern conceptions, solid substances are only those which are crystalline, even though the crystals are small enough to be detected by x-rays only.

Solids behave differently in different crystal planes because these planes may have a different content of the various atomic species that enter into the make-up of the crystal. When a crystal is fractured the surface consists of patches of the various crystal planes, so that the behavior of the solid may be quite different at different points on its surface. A very interesting example is quoted by Desch<sup>(5)</sup>: lead nitrate crystallizes in the shape of tetrahedra from its aqueous solution; upon the addition, in the solution, of methylene blue, the lead nitrate crystals become cubic in shape, and the cube faces which modify the previously grown tetrahedral faces are blue, whereas the tetrahedral faces remain colorless. From this experiment it might be concluded that the dye is adsorbed on the cube faces but not on the tetrahedral faces; this can be correlated to the affinity of the dye for the nitrate radical or for the lead radical, which causes the adsorption to be maximum at a face consisting of but one kind of ions, and minimum at a face of mixed composition consisting of alternate ions of the two kinds.

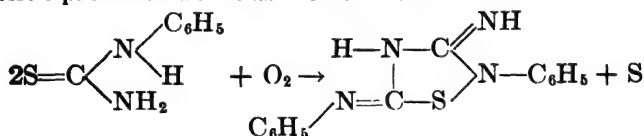


**Catalysis.**—Just as the faces in a crystal may differ from each other in reactivity, so can the edges and still more the corners of a crystal. These facts have been used by Rideal and Taylor<sup>(1)(2)</sup> and Burk<sup>(3)</sup> to explain the mechanism of contact (heterogeneous) catalysis. The enormously greater reactivity in catalyzing certain reactions of the so-called "amorphous metals" obtained through the successive calcination and reduction of some metallic salts is generally ascribed to the presence of a greater proportion of unsaturated metallic atoms. Taylor goes so far as to believe that there exist in the metals used in catalysis some atoms that are less saturated than the atoms at corners, and that it is these extremely reactive atoms which are responsible for the extraordinary behavior of the catalyst.

Although no definite proof has been advanced as yet to show that catalytic reactions occur at the surfaces of minerals dispersed in water, as in flotation, such reactions may well exist, in view of the uncontradicted experimental evidence which shows that adsorption proceeds at solid surfaces in flotation systems, and of the voluminous evidence which shows the close relationship between adsorption and catalysis. A good example of catalysis produced at the surface of a solid dispersed in a liquid is displayed in the case of the catalytic oxidation of phenyl thiourea,



at the surface of blood charcoal, yielding sulfur, and a complex oxidation product known as Hector's base<sup>(7)</sup>.



**The Nature of Adsorption.**—Considerable discussion has arisen as to the nature of adsorption, more particularly whether it is physical, that is, dependent upon forces other than those of chemical reaction, or chemical. Langmuir has claimed that adsorption is a chemical phenomenon and his view has been gaining wider and wider acceptance.

Adsorption phenomena at liquid-gas or solid-gas interfaces are better understood than those at solid-liquid or at liquid-liquid interfaces because the gas is so dilute of matter, when com-

pared with the solid or liquid phases, that it exerts little action, as a phase, upon the course of adsorption phenomena. Adsorption at solid-gas or liquid-gas interfaces depends, therefore, upon the particular affinity of the adsorbate for the solid or liquid, upon the solubility of the adsorbate in the solid or liquid, and upon its vapor pressure. However, the adsorption is substantially independent of the affinity of the adsorbate for other chemical species occurring in the gaseous phase. Adsorption phenomena at liquid-solid or liquid-liquid interfaces are complicated by the fact that the affinity of the adsorbate for the constituents of *each* phase enters into the problem.

In the past few years the notions of adsorption have become broadened in their scope but have lost considerably in definiteness, a number of reactions being now termed adsorptions which would have been called chemical reactions a few years ago, while a number of reactions of an *absorptive* character, in which the absorbent is porous, have ceased to be called adsorptions. At present it is extremely difficult to draw the line between chemical reaction and adsorption. For example, the reaction of certain hydrous silicates (permutites) in removing base-metal ions in exchange for alkali-metal ions is termed *exchange adsorption*, but it might as well be considered a double decomposition; the instantaneous removal of copper for zinc from copper-bearing solutions by sphalerite, which occurs daily in flotation operations, and many other reactions may be considered equally as adsorptions and as chemical reactions. Although some reactions between solids suspended in fluids and the fluids are unquestionably due to adsorption, as for instance the removal of cresol from solution by minerals, while other reactions are distinctly chemical in nature, as for instance the formation of crusts of calcium oxalate on calcite or of lead thiocresylate on cerussite, there are many flotation reactions that lie on the border line and which may be regarded as adsorptions or as chemical reactions. Inasmuch as all chemical reactions must begin as adsorptions of ions or molecules either view is appropriate.



## CHAPTER III

### THE PHASES IN FLOTATION SYSTEMS

The study of flotation, like that of the metallurgy of alloys and of all other complex chemical systems, is best attacked, perhaps, from an itemized study of the various phases that occur in those systems. In the earliest days of flotation, separation between the various minerals was attempted in a system consisting of an aqueous phase, an oil phase, and various solid phases; separation was dependent upon the fact that certain solids have a preferential affinity for an aqueous phase and others for an oily phase. Later, air was introduced in the system, while still retaining the two liquid phases, the aggregate of oiled sulfide particles and air bubbles being separated from the water-wetted gangue particles by its buoyancy which was much greater than the buoyancy of the oil-sulfide aggregates of the earlier processes. In present-day flotation, the oil as a distinct phase has disappeared, and segregation of the various minerals is accomplished through the selective affinity of their surfaces, properly modified by reagents if necessary, for air bubbles and for water. In other words, in the course of its evolution, flotation has passed through three stages: the first featuring two fluid phases, both liquid; the second three fluid phases, one of which was gaseous; and finally two fluid phases, one being a dilute aqueous solution, and the other a gas.

Of the various phases, the gas phase is the simplest, and the solid phases the most complex. The liquid phase, while in appearance very simple, and frequently forgotten in considerations pertaining to modern flotation, is extremely interesting as well as important from a practical standpoint.

#### THE GASEOUS PHASE

The gaseous phase has frequently appeared most important in flotation because it is through the buoyancy of air bubbles that some mineral particles are segregated from the pulp, and gathered in a froth. It seems, however, that its importance has been

exaggerated, as will be apparent when it is considered that air, or any other gas at or near atmospheric pressure, is essentially a vacuum. Thus, 1 liter of air weighs 1.3 g. whereas the same volume of water weighs 1000 g. and that of hexane, one of the lightest of all known liquids, 660 g. The great dilution of gases as compared with liquids or solids is best brought out in the case of water, 1 gram-molecule occupying 30.6 liters in the gaseous state (at 100°C. and 760 mm.) and 0.018 liter in the liquid state, or in the ratio of 1700:1. In other words, if the molecules encountered in 1 sq. cm. of water and of steam were counted, their number would be in the ratio of 1700:1, indicating that any affinity that the water has for some other substance would be much more marked in the liquid than in the gaseous state, at atmospheric pressure. That this is the case in what concerns flotation can be demonstrated by carrying out flotation operations with steam as the gas phase and boiled, air-free water as the pulp medium<sup>(2)</sup>. The apparatus can consist of a cylindrical tank surmounted by a conical portion and provided with a stirrer. The conical portion of the tank is connected to a vacuum pump. Upon evacuation of the tank, steam is generated, rising as mineralized bubbles. The same end can be achieved more easily by heating the pulp under reduced pressure. These experiments indicate that properly treated mineral surfaces adhere to steam bubbles in the presence of water, proving definitely that adherence to bubbles does not depend only upon the chemical composition of the two media between which the mineral must choose, but also upon the concentration of the molecules in the fluid phases. The similarity of the results obtained with steam and with air shows, furthermore, that the composition of the gaseous phase is of relatively little importance.

Although the composition of the gas, considered as a phase, makes little difference, the gas can considerably affect the floatability of minerals if reaction proceeds between the gas molecules and the mineral surfaces, or dissolved reagents, or the water itself. Thus, oxygen is often an oxidizing agent and plays an important part as such in flotation systems; carbon dioxide leads to the formation of calcium carbonate in solutions containing calcium salts which are being aerated; hydrogen sulfide is a strong sulfidizing agent, both from solution in water, and directly upon dry mineral particles, or mineral particles that are attached to gas bubbles. Carbon dioxide and hydrogen sulfide,

furthermore, affect the hydrogen-ion concentration of the aqueous phase. An illustration is found in the change of the pH of distilled water from 7.0 to 6.0 or 6.2 by carbon dioxide in the short time required for the water to cool from the still coils. The subject of the effect of dissolved gases is more properly treated in connection with the discussion of flotation reagents.

### THE LIQUID PHASE

The liquid phase in flotation has always been a dilute aqueous solution, and there are good reasons why it should be: Water is almost universally available and inexpensive; furthermore, it is well suited for flotation work because of its high polarity. There is of course no apparent technical reason why other liquids, such as liquid ammonia should not be used for special flotation operations involving the products of the chemical industries, in which the high value of the products might permit the use of a costly flotation medium. The subject of flotation in non-aqueous mediums deserves investigation from a practical as well as from a theoretical standpoint.

**The Structure of Water.**—Water is such a common substance, and its being composed of hydrogen and oxygen in the atomic proportion of 2:1 has been known so long that its unusual properties are frequently forgotten. Among the most important properties of water that single it out from other substances are: (1) maximum specific gravity in the liquid state at a temperature intermediate between its freezing point and its boiling point; (2) high dielectric constant; (3) great solvent power; (4) low electrical conductivity, yet great ionizing power; and (5) associated state.

The peculiar properties of water are best understood and correlated when some insight is gained into the actual structure of liquid water. For a long time liquid water was considered as a mixture of  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ , and  $(\text{H}_2\text{O})_3$ , in which the proportions of the three kinds of molecules varied with temperature. It has also been known for a relatively long time that water is ionized to some extent into hydrogen and hydroxyl ions in accordance with Eq. (1):



in which the equilibrium between the ions is defined by Eq. (2), the quantities within brackets always denoting concentrations,

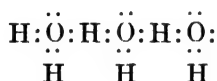
in terms of molality; *i.e.*, in terms of a solution containing 1 gram-molecule of the solute per liter of solution:

$$[H^+] \times [OH^-] = 10^{-14} \text{ at } 25^\circ\text{C.} \quad (2)$$

The associated character of water and its self-ionized condition have been correlated by S. W. Pennycuick<sup>(7)</sup>, who considers that these properties derive from the *asymmetrical* or *polar* character of the water molecule. This, in turn, is best appreciated by a consideration of the association of an oxygen atom with two hydrogen atoms in the light of their electronic constitution. According to Pennycuick, a water molecule, written as a structural formula should be  $H:\ddot{O}:$  rather than  $H:\ddot{O}:H$ , in order that

H

the polar character be emphasized. In other words, the eight valence electrons of the water molecule are arranged in four groups of two each, and are more or less symmetrically placed at the corners of a tetrahedron, whose center is occupied by the oxygen nucleus. The symmetry which at first sight might appear to exist is more apparent than real, due to the presence of the two hydrogen nuclei, or protons, located in the vicinity of two of the four electron groups that surround the oxygen nucleus. Naturally, the electron groups that are not associated with hydrogen protons tend to acquire some, and the electron groups that are associated with hydrogen protons tend to lose them; the combination of these two tendencies results in the formation of chains such as



or ring structures; Pennycuick states that the grouping of six  $H_2O$  molecules yields a particularly stable ring structure, and that this accounts for the fact that ice crystallizes in the hexagonal system.

It must not be assumed that such molecular groupings as occur in liquid water are stable; rather they are prone to break upon impact, or due to their internal energy, and to recombine in a different way. Statistically, however, there are certain definite proportions of the various associations at any time, provided the temperature and pressure remain the same. In the course of the breaking up of the molecular associations, some of the breaks occur in such a way as to leave one of the fragments with an excess of protons and another with a deficiency (from which

it follows that the number of fragments having an excess of protons is exactly equal to that which has a deficiency). These fragments are charged, in accordance with the fact that the proton has a unit charge of positive electricity associated with it; therefore these fragments of the old molecular associations are ions, although they are not generally simple  $H^+$  or  $OH^-$  ions. As a result, the ionization of water is better represented by Eq. (3) than by Eq. (1):



in which  $m$  and  $m'$  need not be whole numbers as they are statistical averages.

**Hydration of Dissolved Ions.**—The fact that the ions into which water breaks up are hydrated is well established, and it has been calculated that, although the hydrated hydrogen ion occurs in pure water in the concentration of  $10^{-7}$ , the unhydrated hydrogen ion, or free proton, occurs only in the concentration of  $10^{-160}$ , a number so much smaller than  $10^{-7}$  as to defy comprehension.

In aqueous solutions there occur, besides hydrogen and hydroxyl, a number of other hydrated ions; indeed there are some physical chemists who consider that hydration of ions is the cause of the formation of ions; that in dissolving in water, a substance breaks up into ions because of reaction with water. For instance, salt would react with water as follows:



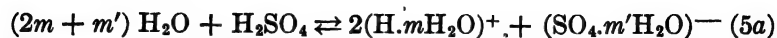
It has been determined that the hydration of some ions, particularly the ions derived from very polar salts, such as the salts of alkali metals and halogens, is very high. One investigator states that in dilute solutions of lithium chloride each lithium ion carries 21 molecules of water.

The concept of ions as more or less abundantly hydrated matter in a reactive form is important for a full understanding of flotation: hydrated ions under certain conditions adhere to the surface of minerals which thus become coated with a film of water and are therefore wetted by it.

In a mixture of two miscible liquids such as ethyl alcohol and water, one of the liquids is called the solvent and the other the solute; which is which is hard to tell, for it might be considered that pure water or pure alcohol is the starting point and that the other substance is gradually added to it. In the same way, the mixture of two slightly ionized substances such as sulfuric



acid and water may result in highly ionized solutions: it is difficult to decide whether the ions are hydrated hydrogen and hydrated sulfate ions from the sulfuric acid, or hydrogen-sulfated hydrogen and hydrogen-sulfated hydroxyl ions from the water, or both.



In this connection it is interesting to note that concentrated sulfuric acid wets pyrite but that, upon the addition of water to the acid, the fluid ceases to wet the mineral, possibly because the liquid has become polar, while the mineral has remained non-polar. The same thing is true of realgar which is wetted by alcohol, but is not wetted by mixtures of alcohol and water.

Just as the polarities of sulfuric acid and water are very much increased by mixing these two liquids together, so the polarity of sodium chloride and that of water are increased by dissolving them in each other, a strong solution of salt, for instance, being a better conductor of electricity than solid sodium chloride or water.

**Substances Molecularly Dissolved in Water.**—All substances which dissolve in water do not ionize, although a large number are probably hydrated to some extent. These substances are generally much less polar than the substances that ionize, and comprise the ordinary gases of the atmosphere and most organic compounds. It frequently happens among heteropolar organic compounds that one part of the molecule is much more likely to hydrate than another part. An instance is found in the case of alcohol, which is an associated liquid in the pure state, and which dissolves in water with great avidity and evolution of heat, these effects being the result of the hydration of the OH-group characteristic of alcohol molecules.

Besides the substances which ionize on dissolving in water, and those which form molecular dispersions there are a number that because of incomplete molecular dispersion or large size of molecules display colloidal properties. The latter may be regarded equally as belonging to the liquid phase or as a different phase suspended in the liquid phase.

**Hydrogen-ion Concentration.**—One of the most important factors affecting the performance of flotation systems is the hydrogen-ion concentration of the pulp. As has already been

stated, water ionizes into hydrated hydrogen, and hydrated hydroxyl ions. The product of the concentrations of these ions is constant (the law of mass action of Guldberg and Waage), that is:

$$[(H.mH_2O)^+] \times [(OH.m'H_2O)^-] = 10^{-14}. \quad (6)$$

If there is present in water some substance which ionizes so as to give rise to more  $(H.mH_2O)^+$  ions, the total number of these ions is increased, and the total number of the  $(OH.m'H_2O)^-$  ions is decreased in accordance with Eq. (6). Such solutions are known as acid solutions. Conversely, solutions giving rise to additional hydroxyl ions cause a decrease in the total hydrogen-ion concentration, and are known as alkaline solutions.

For practical purposes the extreme limits of hydrogen-ion concentration, in water, are  $10^{+1}$  and  $10^{-15}$ , the first corresponding to a ten-molar monoacid solution that is completely ionized, and the second to an equally strong monoalkaline solution. In flotation work, the limits between which the hydrogen-ion concentration may vary are more restricted,  $10^{-3}$  and  $10^{-13}$  being ample limits.

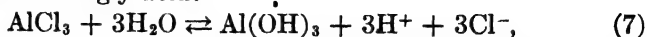
In order to simplify the terminology whereby the hydrogen-ion concentration is expressed, Sørensen<sup>(1)(4)</sup> has introduced a special scale which he termed the *pH scale*, in which the numerical pH value is equal to the exponent, with the sign changed, of the hydrogen-ion concentration when expressed as a power of 10; or, the pH is equal to the logarithm to the base ten of the hydrogen-ion concentration, with the sign changed.

In solutions near neutrality, small additions of acidic or alkaline substances produce great changes in pH. This is readily appreciated by a consideration of the increase in hydrogen-ion concentration necessary, for instance, to change the pH of pure water from 7 to 6:

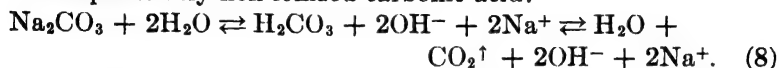
$$d(H)^+ = 10^{-6} - 10^{-7} = 9 \times 10^{-7}.$$

The great change in pH following the addition of little reagent is illustrated by the difficulty in getting distilled water having a hydrogen-ion concentration of  $10^{-7}$ : the carbon dioxide from the air dissolves, combines with water to form carbonic acid and gives rise to a sufficient concentration of hydrogen ions to bring the pH in the range from 6.0 to 6.4. On the other hand, a considerable amount of acidic material is necessary to change the pH from 1 to 0, or from 14 to 13.

Most salts do not yield neutral solutions, that is solutions whose pH is exactly 7, even when made from carbon-dioxide-free distilled water. This is because they react with the water (hydrolyze) to form one weakly acid or alkaline product together with one strongly acid or alkaline product. Thus, aluminum chloride solutions are strongly acid:



but sodium carbonate solutions are alkaline, due to the formation of comparatively non-ionized carbonic acid:



When they are present in water, salts such as aluminum chloride or sodium carbonate prevent sudden changes in pH upon addition of other substances: the addition of hydrochloric acid to a solution containing already some aluminum chloride does not have as much effect as it would have on a solution of the same pH obtained through the use of hydrochloric acid alone. This is because the addition of hydrochloric acid to a solution of aluminum chloride represses the hydrolysis of the salt, reducing the concentration of hydrogen ion resulting from that cause, so that the total hydrogen-ion concentration falls short of the original concentration plus that of the added acid. In the same way, addition of an alkali to aluminum chloride solutions increases the hydrolysis so that the full effect of the alkali is not obtained. Such action as that described for aluminum chloride, and which occurs with all salts that give solutions that differ from neutrality, is known as *buffer action*, and is important in flotation operations.

### THE SOLID PHASES

In contrast to the fact that there is but one gas phase and one liquid phase in modern flotation operations, the number of solid phases may be very large, and they may occur in relatively complex association. For instance, some solid particles may be of one mineral species only, and therefore contain one solid phase only, whereas others may contain several. For the present time middling particles will be forgotten (but see Chap. VII) and it will be assumed that all the mineral grains have been freed, that is that each particle contains but one solid phase.

**Polarity and Capacity for Hydration of Minerals.**—The majority of the mineral species encountered in flotation systems are non-ionized substances because they must, of necessity, be

relatively insoluble in water. Ionized substances have generally a greater solubility in water than non-ionized substances (this can be traced to the ionizing properties of water) and are therefore rarer as mineral substances. Outstanding examples of ionized substances encountered in flotation are fluorite ( $\text{CaF}_2$ ) and calcite ( $\text{CaCO}_3$ ).

Of the non-ionized solids encountered in flotation some are capable of becoming ionized by hydration; others are not. An example of a non-ionized substance capable of becoming hydrated is feldspar. Microcline (generally written  $\text{KAlSi}_3\text{O}_8$ ), for instance, can be regarded as  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , in which each oxide is capable of becoming hydrated to  $\text{KOH}$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{H}_2\text{SiO}_3$  (or  $\text{H}_4\text{SiO}_4$ ), respectively. Of the non-ionized substances practically incapable of hydration, the best examples are found in the case of the metals (oxidation of the metals is disregarded as it entails a transfer of electrons), of intermetallic compounds, of intermetalloid compounds, of sulfides, selenides and tellurides of the base and noble metals, and of certain iodides.

**Polarity and Floatability.**—*The polarity or non-polarity of minerals, together with the capacity for hydration which transforms the surface of certain otherwise non-polar minerals into polar areas, controls their wettability by water and, ultimately, their flotation or non-flotation.* This is a natural consequence of the difference or the similarity in the properties of the surfaces of the minerals and the water. Consider, for instance, a particle of fluorite in equilibrium with a saturated solution of calcium fluoride in water otherwise pure. There is a constant exchange of calcium and fluoride ions between the two phases; and these ions being hydrated in the liquid phase bring to the surface of the mineral some relatively adherent water. Also, even if such a migration of ions did not exist, the ions of the crystal at the surface of the mineral would allow their tendency to hydrate to be manifested by retaining (adsorbing) water molecules to their surface: *a transitional layer exists between the crystal and the solution which cements water to the mineral.* The same considerations hold for calcite suspended in water, because calcite is made up of  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  ions,<sup>(13)</sup> which become hydrated when in contact with water.

Although quartz may appear to be a non-polar substance, it hydrates *very* readily as is suggested by the difficulty which is experienced in removing all the water from a silica gel (prolonged

heating to a white heat is necessary)<sup>(6)</sup>, and by the fact that quartz has a substantial heat of wetting. Accordingly, the surface of a quartz particle suspended in water really consists of hydrated silicic acid molecules, so that in the case of the particle of quartz suspended in water, just as in the case of the particle of fluorite or calcite, a transitional layer between the solid and the liquid exists which is bonding the two phases together. The case of a non-polar solid which cannot be hydrated is totally different. Consider, for instance, sulfur, which does not hydrate: the phases must be *bound discontinuously*.

**Contact Angle.**—The relations between the two fluid phases and the solid phase can be viewed with respect to the tendency exhibited by a gas to displace water from contact with a mineral surface. This is best expressed in terms of the *contact angle*

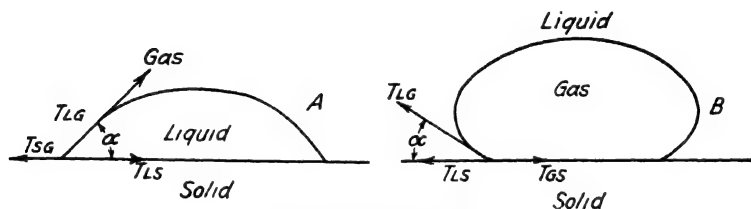


FIG. 3.—Contact angles.

A liquid drop resting on a solid. B gas bubble adhering to a solid

between drops of water placed upon the surface of the solid or of submerged gas bubbles upon the water-solid interface. These relations were mathematically discussed by Reinders<sup>(9)</sup> who calculated that the cosine of the inside angle made by the resting drop, or the cosine of the outside angle made by the adhering bubble and the solid surface, is related as follows to the surface tensions involved (see Fig. 3):

$$\cos \alpha = \frac{T_{SG} - T_{LS}}{T_{LG}}$$

in which  $T_{SG}$ ,  $T_{LS}$ , and  $T_{LG}$  are the surface tensions between pairs of adjacent phases. The Reinders equation has been experimentally verified in the case of two liquids and a gas but not in the case of one solid, one liquid, and a gas, because no means of measuring the surface tension of solids have yet been devised. The Reinders equation while probably correct in cases involving solids is of no practical importance at the present time, although it has been useful in the early days of flotation as a qualitative guide in expressing a relationship between contact angles and

flotation results<sup>(11)</sup>. Sulman made a detailed study of contact angles<sup>(10)</sup> and discovered that they were subject to a phenomenon which he called hysteresis upon whose magnitude he considered flotation phenomena to depend. It would be desirable to extend his investigations in the light of modern flotation data.

**Surface Alterations on Minerals.**—The importance of the surface alterations of minerals has never been sufficiently emphasized as a factor of paramount importance in determining the flotation of minerals in the absence of reagents other than frothing agents. The discordant results obtained in practice and in testing were largely the result of a comparison of data obtained with mineral surfaces that could not be compared. The first sulfide to be studied in a clean, reproducible surface was pyrite<sup>(3)</sup>. As the result of this work, pyrite was shown to be very floatable when pure, but poorly floatable when materially oxidized. Later, work with other sulfides was done with clean surfaces whenever possible. At this point, it might be well to emphasize that by a clean surface is not meant a surface that is absolutely free of any alteration, but rather a surface that is as clean as can be made, and one that is reproducible.

**Reactions Involving a Solid Phase.**—Considerations pertaining to surface alterations on minerals bring up the most interesting and difficult subject of reactions involving the solid state. These reactions are best studied in contrast to reactions in the liquid state.

Reactions involving the liquid state only are of two types: those in which the reactants are ions and those in which the reactants are molecules. Reactions of the latter type are common in organic chemistry and are catalyzed by certain special constituents, frequently the hydrogen or the hydroxyl ion. Reactions between ions are generally very rapid and depend essentially for their completion upon the concentration of each reacting species and of the reaction products.

Reactions involving a solid phase differ from those in the liquid state in that the extent of the solid surface takes the place of the concentration of one of the reactants in determining the rate of the reaction. The problem of the disposal of reaction products does not exist in reactions occurring in a liquid phase because the perfect dispersion of the reacting substances makes it unlikely for a situation to arise in which diffusion is a major factor. In reactions involving a solid phase, and unless the product of

reaction is dissolved in the liquid phase, in which case diffusion in the liquid phase is the only complicating feature, there develops a material hindrance to a continuation of the reaction. If the reaction product is an adherent coating<sup>(8)</sup>, that is one which sticks to the surface of the solid because of similarity in lattice, the reaction is practically stopped except for the diffusion in the solid state; if the coating is loose, the reaction may only be damped in relation to the rate at which the coating is shelled off or penetrated by the solution.

**Nature of Alterations at Mineral Surfaces.**—Minerals in flotation pulps are already more or less altered at their surface by reactions with the ore solutions or with soluble ingredients developed in the course of milling. As a result, the flotation systems are still more complicated than one might be led to believe from the large number of phases present in them.

In a study of the surface alterations of minerals in the course of mining, storing, and dressing, it is well to consider first the agencies that bring about these changes: water and air. During mining, storing, and dressing, ores are damp but accessible to air (as a gas or in solution in water), so that the two agencies of surface alteration work hand in hand. Of the constituents of the atmosphere, oxygen and carbon dioxide are the most important, as they are, in conjunction with water, the prime factors required to form oxides, sulfates, carbonates, and hydroxides. Those minerals in ores which are not capable of forming reaction products with the atmosphere and water are generally unaltered except for the solution of some portions of the mineral surface in preference to that of other parts; they include oxides, carbonates, sulfates, silicates, which can all be regarded as substances having reached or approaching the maximum state of oxidation; they include also certain unoxidized substances the solubility of which in water is extremely minute and which are not oxidized except at high temperature, for example, graphite. Minerals that are not approaching the maximum state of oxidation form reaction products with oxidizing agencies more or less rapidly; it happens that most floatable substances belong in this group, so that a great range in floatability may be presented by the same mineral in various ores or even in the same ore at various stages of oxidation.

**Mechanism of Sulfide Oxidation.**—The mechanism of the oxidation of sulfides is not well understood, and considerable

divergence of opinion exists as to the mechanism of the oxidation and even as to the facts of the case. Pyrite, for instance, is one of the most readily oxidizable sulfides in nature, yet it is very difficult to oxidize in the laboratory, either through the action of sulfuric acid and oxygen, or through the action of oxygen in water. Galena surfaces oxidize to lead sulfate in a very short time, even under water; the depth of the oxidation is slight, and the crust of lead sulfate or of basic lead sulfate which is formed appears to protect the galena from further oxidation just as the basic zinc carbonate crust formed by weathering on galvanized iron protects the metal from further alteration. Chalcocite is known to oxidize very easily to basic copper carbonates, and is often associated in nature with malachite and azurite. Chalcopyrite and sphalerite seem less susceptible to alteration than the aforementioned sulfides, and molybdenite is rarely altered.

It is of more than academic interest to know how these oxidations proceed—whether, for instance, they occur uniformly upon the surface of the mineral or in patches. The bulk of the evidence favors the view that oxidation does not proceed uniformly. Thus, even though the amount of oxidation on the surface of a sulfide may exceed that amount which would be required to paint the whole surface uniformly to the depth of one atomic diameter, the mineral may exhibit a substantial floatability in the presence of a frother alone, because of the presence of highly floatable bare sulfide patches; in a sense such a particle can be considered as a middling of highly floatable sulfide and non-floatable oxidized coating. Reactions involving the solid state frequently proceed first at certain patches. This is illustrated by the roasting of limestone to make lime, in which case carbon dioxide is driven off from certain spots first, the decarbonation proceeding from the centers of decarbonation in preference to proceeding from fresh centers<sup>(5)</sup>. A partly oxidized sulfide surface may likewise be viewed as a patchwork of sulfide and oxidized portions, the proportions of the two constituents determining the floatability of the mineral.

**Surface Alterations Other than Oxidation.**—It has been observed that certain results having practical value were obtained with certain ores, which failed to be obtained with ores of similar composition, or that the results obtained in the laboratory with simplified flotation systems were of no value in practice. These discrepancies have generally been caused by the presence in some



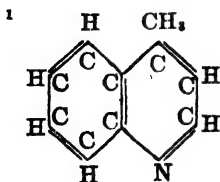
flotation systems of soluble constituents which altered the surfaces of certain minerals, modifying their floatability. One interesting example which can be recalled to illustrate this statement is in connection with the flotation of chalcocite and pyrite with methyl quinoline.<sup>1</sup>

That reagent, when used to the extent of 0.04 lb. per ton gives a complete recovery of the chalcocite; on pyrite the recovery is but 8 or 10 per cent. From these data one would expect chalcocite to float away from pyrite in the treatment of a pulp containing the two minerals. But the opposite happens. This is due to soluble copper (derived from the chalcocite) in amount sufficient to increase the floatability of the pyrite beyond that of the chalcocite, possibly by forming a sulfide-copper coating at the surface of the pyrite. The effect can be corrected by making the solution sufficiently alkaline so that the copper-ion concentration is not sufficient to activate the pyrite in the short time the ingredients are in contact.

In the same manner, the joint presence of sphalerite and copper carbonate results in the flotation of much sphalerite under conditions which otherwise do not allow sphalerite to float. The lack of selection between the minerals is to be ascribed to the transfer of copper ions from the malachite to the sphalerite.

**Native Floatabilities of Minerals.**—If the causes of surface alteration, such as oxidation, or modification of surface composition by soluble natural ingredients are eliminated, the sequence of decreasing floatability of ordinary minerals can be considered as being, approximately, as follows:

1. Pure metals and metalloids.
2. Intermetallic and intermetalloid compounds.
3. Sulfides of the metals nearest sulfur in the periodic table.
4. Sulfides of the metals furthest from sulfur in the periodic table.
5. Non-acid-forming oxides of the metals nearest to the dividing line between metals and metalloids in the periodic table.



6. Compound oxides and oxides of the metals far removed from the dividing line between metals and non-metals in the periodic table.

The first three classes of compounds have metallic, adamantine, or resinous luster; and the last three range from substances having a resinous luster to substances having a glassy or earthy appearance, thus corroborating the convenient practical rule given 10 years ago by Taggart<sup>(12)</sup> who stated: "Almost any ore consisting of a mineral of metallic, resinous, or adamantine luster associated with the usual rock-forming minerals, can be concentrated by flotation."

The surface oxidation of most of the pure metals, and a great many sulfides somewhat changes the order of floatability, so that, in practice, the following substances, only, can be floated without the addition of a collector.

Generally Floated upon Addition of a Frother Only:

- Carbon (graphite, diamond).
- Sulfur.
- Molybdenite.
- Realgar.
- Carborundum.
- Iodine.

Frequently Floated upon Addition of a Frother Only:

- Chalcopyrite.
- Enargite.
- Galena.
- Jamesonite.
- Stibnite.
- Coal.
- Gold.

Rarely Floated upon Addition of a Frother Only:

- Native copper.
- Pyrite.
- Chalcocite.
- Native silver.



## CHAPTER IV

### COLLOID SYSTEMS

Considerable interest attaches to the study of *colloids*. Graham<sup>(7)</sup> who coined the word, meaning glue-like, and who contrasted *colloids* with *crystalloids*, believed that some substances are always colloidal and others always crystalline. This view has been superseded by the belief that colloidal properties can be acquired by any substance in the proper state of dispersion in a suitable medium. In general, it can be said that a colloid is a system consisting of several phases arranged so that one or more are dispersed in another. Thus a "solution" of starch in water is a colloidal system; so is a piece of cheese. In the same way, a finely dispersed mineral in water may be considered as a colloidal system.

**Particle Size of Dispersed Phases.**—There is some divergence of opinion as to what constitutes the upper size limit of the dispersed particles in a colloidal system. It would, perhaps, be safe to assume with Zsigmondy<sup>(16)</sup> that if the dispersed particles are fine enough to be little inclined to settle in the dispersing medium, but markedly affected by Brownian movement (molecular bombardment), the system is colloidal. For minerals suspended in water this upper size limit for the dispersed phase may correspond to about 0.5 to 1.0 micron.

The lower size limit for colloids is also ill defined; the general consensus of opinion is that dissolved substances can be dialyzed, that is, filtered through a porous medium whose pores approach the usual size of ions and molecules, but that colloiddally dispersed substances cannot be dialyzed. That size at which dialysis ceases to be possible is about 0.002 to 0.003 micron. Accordingly, it would appear that the size of colloidal dispersion covers a 300- to 500-fold range.

The large majority of flotation pulps are ground so that most particles are finer than 200 or 300 microns, and so that a portion of the pulp feels slimy; it is not advisable, however, to consider the pulp as a whole as a colloidal system because the largest particles

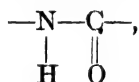
are much too coarse to come within the scope of our definition of colloidal particles: perhaps only 1 to 5 per cent of the pulp is fine enough to be reckoned as a colloid (see Chap. VII for data). The colloidal portion of ore pulps may represent but a minor portion of the pulp mass but it accounts for a large portion of the total solid surface present so that a consideration of colloidal properties is of paramount importance.

**Types of Colloids.**—Although almost all substances may be made to take the form of a colloidal dispersion, certain substances seem to form colloidal solutions naturally, whereas others seem to form them only under suitable conditions. Extreme examples are gelatin and gold. Colloidal gold has been known for a long time, but it has never been found possible to make it by immersing a gold foil in water; on the other hand, a strip of gelatin immersed in water swells by taking up water, and finally forms a solution of colloidal gelatin. A gold *sol* (colloidal solution) is obtained only when very fine gold particles, in the process of growth from molecular dispersion, are prevented from growing further by the adherence upon their surface of hydrated ions (such as the  $[\text{Cl} \cdot m\text{H}_2\text{O}]^-$  ions produced by the oxidation of aurochloric acid) or of colloids of the gelatin type, which for that reason are known as *protective colloids*. Colloids of the gelatin type are also known as *lyophilic*, meaning "liking water," whereas gold is typical of substances forming *lyophobic* colloids.

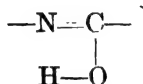
Lyophilic colloids can be regarded as the only genuine colloids, for they tend to form colloidal solutions of their own accord. They are generally organic compounds having large, clumsy molecules composed of various radicals possessing different properties. Their colloidal properties are the result of their heterogeneous character, some of the radicals entering into their make-up being very soluble in water, others much less so. As a result, protective colloids arrange themselves as small units or micelles in which the polar part of the molecules is oriented toward the water phase, and the non-polar part away from it, that is, toward the interior of the micelle. To be good protective colloids, the unassociated molecules of lyophilic colloids must present several polar groups; a polar radical must be available for attachment on the protected particles, and another must be available for hydration. If protective colloids are present in solution, lyophobic particles become coated to a greater or lesser extent, and thereby acquire toward the rest of the system the properties

of the protecting substance. This coating prevents additions of lyophobic material to the coated particles, and forces new nuclei to form; grain growth by the adherence to each other of similar lyophobic particles is also reduced: the result of adding protective colloids is therefore to retard or stop the otherwise natural evolution of a system in progress toward a stable equilibrium.

Examples of colloids that are typically protective are the glues, gelatins, albumens, and the gums, the molecules of which all contain several polar groups. Gelatin, for instance, can be represented by the general formula  $\text{NH}_2\text{.R.COOH}$  in which the radical R stands for a complex structure<sup>(1)</sup> containing the polar group  $\text{—COHN—}$ , which may exist in the keto form



or in the enol form,



Gelatin therefore contains several polar groups besides the  $\text{NH}_2$  and  $\text{COOH}$  groups.

Certain other lyophilic colloids are protective only if used in large amount. Colloids of this type have their molecules polar in one part and non-polar in another. If used in small amount, so that there is insufficient colloid to form thick layers at the surface of the particles to be protected, a first layer forms in which the molecules are oriented with their polar part toward the particles to be protected, and their non-polar, water-repellent end toward the liquid phase; under these circumstances the colloid is far from being protective, causing coagulation of the coated particles. This, for instance, is what happens to minerals upon addition of small amounts of soap. If, on the other hand, the coating of soap molecules is thick, the molecules of the latter may arrange themselves as a first layer with the polar end toward the solid to be protected and the non-polar end outward, and as a last layer with the polar end toward the water. Particles coated in such a fashion present the same properties as a droplet of soap in water, that is, they appear polar, and therefore are wetted. The detergent action of soap is explained in this fashion<sup>(5)</sup>.

**Stabilization of Colloids by Ions.**—Protective colloids insure comparatively irreversible protection of lyophobic colloids from

**coagulation.** The same end is achieved in a reversible manner through the presence of certain ions which adsorb at the surface of the lyophobic colloid, and cause it to be wetted because of the water of hydration which the ions have associated with them. A good example is the protection of base-metal sulfide sols by hydrogen or sulfide ions.

The adsorption of ions at the surface of solids is frequently a manifestation of the tendency of the ions in solution to form an insoluble precipitate with one of the ions in the solid. The classic illustration is found in the sign of the charge at the surface of silver iodide micelles when silver iodide is precipitated from silver nitrate and potassium iodide with excess of silver and excess of iodide, respectively<sup>(12)</sup>. If an excess of silver ion is present the precipitate is positively charged due to adsorption of silver ions; if an excess of iodide ions is present the precipitate is negatively charged due to adsorption of iodide ions, and if the quantities of silver and iodide ions are substantially equivalent the precipitate coagulates readily.

Most inorganic precipitates, particularly those that are very little soluble, can be obtained in colloidal form, protection being obtained by some ion in solution. The formation of colloidal precipitates is favored by conditions under which the precipitate is little soluble, because these conditions compel the establishment of a large supersaturation and the formation of many nuclei. The formation of colloidal sols is also favored by certain salts whose positive and negative ions may have different tendencies to adsorb on the surface of the micelles of the precipitate. Conversely, colloidal precipitates can be made to flocculate or to grow to filtrable crystals by the expedient of boiling for a material length of time. Boiling increases the solubility, thus favoring crystal growth; it is also probable that it decreases ion adsorption by increasing the polarity of the fluid phase (the ionization constant of water at boiling is almost one hundred times as large as at room temperature). The easiest way to flocculate colloidal precipitates is by adding, in solution, certain salts which counteract the stabilizing effect of the ions already present in the system.

**Flocculation and Dispersion.**—Suitable control of *flocculation* and of the converse, *dispersion*, is of great importance in ore dressing, particularly in the classification of finely ground pulps, in thickening, in filtering, and in flotation.

Flocculation or coagulation can be defined as the clumping to form loose aggregates of particles previously suspended in water. The term flocculation has been used in flotation to refer to the clumping of concentrate particles with gas bubbles as well as to the clumping of particles in the absence of gas bubbles; in this book, the term flocculation is restricted to the phenomenon that obtains in the absence of gas bubbles.

If similar particles of a size sufficiently small to be substantially unaffected by sedimentation are dispersed, it may be inferred that the dispersion is very dilute or that the particles are hydrated, or that they are similarly electrically charged. Frequently dispersion can be ascribed to a combination of these causes. Pulp in the dispersed state are unstable, or at best metastable (second law of thermodynamics), and in due course of time coagulation sets in. Dispersion can generally be restored by chemical means, such as the addition of dispersing salts or the addition of protective colloids or by mechanical means such as the shearing of floccules in colloid mills.

The importance of pulp dilution as a factor affecting dispersion is indicated by Tables 4 and 5. In Table 4, the volumetric dilution  $D$  (ratio of volume of liquid to volume of solids) is related to the ratio  $y$  of the net average distance between particles to the average particle diameter.<sup>1</sup> Table 4 shows that interparticular

<sup>1</sup>Let

$V$  = total volume.

$V_1$  = volume of liquid.

$V_2$  = volume of solid.

$D$  = dilution.

$a$  = average particle diameter.

$x$  = average distance between particle centers.

$n$  = number of particles in volume  $V$ .

Then:

$$V = V_1 + V_2. \quad (1)$$

$$D = \frac{V_1}{V_2}. \quad (2)$$

$$V_2 = na^3. \quad (3)$$

$$V = nx^3. \quad (4)$$

From (3), (4) and (1):

$$\frac{V_1 + V_2}{V_2} = \left(\frac{x}{a}\right)^3 \quad (5)$$

Combining (5) and (2):

$$D + 1 = \left(\frac{x}{a}\right)^3 \text{ or } \frac{x}{a} = \sqrt[3]{D + 1}.$$



distances change much slower than the corresponding volumetric dilutions.

TABLE 4.—RELATION OF VOLUMETRIC PULP DILUTION TO DISTANCE BETWEEN PARTICLES

Dilution, $D$ (Ratio = $\frac{\text{Volume of water}}{\text{Volume of solids}}$ )	Average net distance between particles Ratio $y = \frac{\text{Average particle diameter}}{\text{Average net distance between particles}}$
1	0.26
2	0.44
3	0.59
4	0.70
6	0.91
10	1.20
25	1.96
100	3.67
250	5.31
1,000	9.0
2,500	12.6
10,000	20.6
100,000	45.5
1,000,000	99.0

Flocculation cannot take place unless the particles come in close contact with each other. Particles are brought in contact with each other by Brownian movement. According to Einstein<sup>(4)</sup> and von Smoluchowski<sup>(13)</sup>, quoted by Kruyt<sup>(9)</sup>, the average displacement  $\Delta x$  of a particle, due to Brownian movement, is related to time  $t$ , the gas constant  $R$ , absolute temperature  $T$ , the Avogadro number  $N$ , viscosity of dispersed medium  $\mu$ , particle diameter  $a$ , by Eq. (7)

$$\Delta x = \sqrt{t} \sqrt{\frac{RT}{N} \frac{2}{3\pi\mu a}}, \text{ in c.g.s. units.} \quad (7)$$

From this equation can be obtained Eq. (11):<sup>1</sup>

$$\theta = 0.3a^3 \frac{y^2(y+1)}{y+1 - \sqrt{y(y+2)}}, \quad (11)$$

The net average distance between particles is clearly less than  $x$  by the amount  $a$ , so that the ratio  $y$  of the net distance between particles to the particle diameter is

$$y = \frac{x}{a} - 1 = \sqrt[3]{D} + 1 - 1. \quad (6)$$

<sup>1</sup> Derivation of Eq. (11):

Although all particles are moving, for purpose of analysis it may be assumed that of two particles one is not moving (reference point) and that the other particle is. If each particle were to move by  $\Delta x$  with reference

in which  $y$  denotes the ratio between the average distance apart of particles and their diameter,  $a$  the diameter of the particles in microns, and  $\theta$  the average time required for a particle to travel to one of its neighbors. This time  $\theta$  can be considered as propor-

to water, the probable motion with respect to each other would be  $\Delta x \sqrt[3]{2}$ . Hence, substituting  $ya$  for  $\Delta x \sqrt[3]{2}$  and squaring Eq. (7) we get:

$$y^2 a^2 = \frac{t \cdot 2RT}{3 \sqrt[3]{4 \cdot \pi N \mu a}}.$$

Hence:

$$t = \frac{3 \sqrt[3]{4 \pi N \mu}}{2RT} a^2 y^2. \quad (8)$$

Equation (8) gives the time required for a particle to travel far enough to meet a particle located at a distance from it equal to the average distance apart between particles.

If after traveling for time  $t$ , the moving particle were to meet the assumed stationary particle,  $t$  would be the time for flocculation. But the traveling particle may not have traveled in the proper direction. If it has not traveled in the proper direction, repetition of the process will have to take place. If therefore  $p$  is the probability of a single particle contacting with

another after traveling for time  $t$ , and if there are  $4\pi$  particles  $\frac{4\pi a^2(y+1)^2}{a^2(y+1)^2}$

at the distance  $ay$  from the particle under consideration, the statistical average time  $\theta$  for flocculation is

$$\theta = \frac{t}{4\pi p}. \quad (9)$$

The probability  $p$  of the particle being properly directed to meet another particle is the ratio of the surface of a segment of a sphere to the surface of the sphere, the segment being contained within a cone of revolution having the center of the sphere of radius  $(y+1)a$  as its apex and generated by a point on the surface of the sphere at a distance  $a$  from the axis of revolution.

The area of the sphere is  $4\pi(y+1)^2 a^2$ ; the area of the segment is

$$(y+1)a \cdot (1 - \cos \alpha) 2\pi(y+1)a,$$

in which  $\alpha$  is the apical angle of the cone. But

$$\sin \alpha = \frac{a}{(y+1)a} = \frac{1}{y+1},$$

hence

$$\cos \alpha = \frac{\sqrt{y(y+2)}}{y+1},$$

and

$$p = \frac{2\pi a^2(y+1)[(y+1) - \sqrt{y(y+2)}]}{4\pi(y+1)^2 a^2} = \frac{y+1 - \sqrt{y(y+2)}}{2(y+1)}. \quad (10)$$

tional to the time required for flocculation to take place. Indeed, if every encounter between particles resulted in their sticking to each other,  $\theta$  would represent the time of coagulation. In reality, due to the presence of adhering ions at the surface of the particles, the time of coagulation can be represented by Eq. (12) in which  $K$  is a factor greater than 1:

$$\theta' = 0.3Ka^3 \frac{y^2(y+1)}{y+1 - \sqrt{y(y+2)}} \quad (12)$$

These considerations are in agreement with Kruyt's<sup>(9)</sup> conception of coagulation as involving a *probability of collision* (Eq. [11]), as well as a *probability of adhesion* (factor  $K$ ).

Table 5 presents the approximate relation between the critical size above which flocculation is not possible even with completely discharged particles with varying dilutions and depths of settling (as long as dilution is not appreciably affected by sedimentation).

TABLE 5.—RELATION OF CRITICAL (MAXIMUM) FLOCCULATING SIZE TO DILUTION AND SETTLING DEPTH (TIME)

Dilution, $D$	Ratio of inter- particular dis- tance to particle diameter, $y$	Maximum particle size, $a$ (microns), for flocculation if settling depth is		
		1 cm.	10 cm.	100 cm.
1	0 26	7 2	10 4	18 2
2	0 44	5 5	8 7	13 8
3	0 59	4 7	7 5	11 8
4	0 70	4 2	6 7	10 5
6	0 91	3 6	5 7	9 0
10	1 20	2 9	4 7	7 3
25	1 96	2 2	3 5	5 5
100	3 67	1 42	2 3	3 6
250	5 31	0 94	1 49	2 4
1,000	9 0	0 73	1 16	1 8
10,000	20 6	0 39	0 62	0 98

From Eqs. (8), (9), and (10):

$$\begin{aligned} \theta &= \frac{3\sqrt[3]{4\pi N\mu}}{2RT} \cdot a^3 y^2 \cdot \frac{2(y+1)}{4\pi[y+1 - \sqrt{y(y+2)}]} \\ &= \frac{3\sqrt[3]{4}}{4} \frac{N\mu a^3}{RT} \frac{y^2(y+1)}{y+1 - \sqrt{y(y+2)}}, \text{ in c.g.s. units.} \\ \theta &= 0.3a^3 \frac{y^2(y+1)}{y+1 - \sqrt{y(y+2)}}, \end{aligned} \quad (11)$$

in which  $a$  is in microns and  $\theta$  in seconds.

The figures of Table 5 were obtained by equating  $\theta$ , obtained from Eq. (11) with the time obtained from Stokes' law<sup>(14a)</sup> for the sedimentation of fine particles.<sup>1</sup> They were directly obtained from Eq. (13)

$$a = 5.06 \sqrt[5]{l \left[ \frac{y+1 - \sqrt{y(y+2)}}{y^2(y+1)} \right]^{3/5}}, \quad (13)$$

in which  $a$  is the particle diameter of maximum flocculating size,  $l$  is the settling distance, and  $y$  the ratio of the distance between particles to the particle diameter.

Table 5 shows that for substantially spherical gangue particles flocculation may begin in flotation pulps only if the particles are smaller than 3 to 8 microns. Since there are a great many particles finer than  $3\mu$  (perhaps 5 to 10 per cent of the total mass of solids in average flotation pulps), and these particles average much under  $1\mu$  in diameter, it is clearly seen why they may flocculate so readily. In flotation pulps, too, a large propor-

<sup>1</sup> According to Stokes:

$$V = \frac{1}{18} g a^2 \frac{\sigma - \delta}{\mu}, \text{ in c.g.s. units,}$$

in which  $V$  is the velocity,  $g$  the acceleration of gravity,  $a$  the particle diameter,  $\sigma$  the specific gravity of the solid,  $\delta$  the specific gravity of the fluid, and  $\mu$  the viscosity of the fluid.

But

$$V = \frac{l}{\theta}$$

in which  $l$  is the settling depth in centimeters. Hence

$$\frac{l}{\theta} = 9 \times 10^3 a^2,$$

in which  $a$  is in centimeters, or

$$9 \times 10^{-5} a^2$$

in which  $a$  is in microns. Hence:

$$\theta = \frac{l}{9 \times 10^{-5} a^2} = 0.3 a^2 \frac{y^2 (y+1)}{(y+1) - \sqrt{y(y+2)}}$$

Therefore

$$\begin{aligned} a^2 &= \frac{0.3l}{9 \times 10^{-5}} \cdot \frac{y+1 - \sqrt{y(y+2)}}{y^2(y+1)} \\ &= 0.033 \times 10^5 \frac{y+1 - \sqrt{y(y+2)}}{y^2(y+1)} \\ a &= 5.06 \sqrt[5]{l \frac{y+1 - \sqrt{y(y+2)}}{y^2(y+1)}}. \end{aligned} \quad (13)$$

tion of the very fine particles are made up of the secondary minerals that result from the decomposition of feldspars. These particles are very thin, flaky, and possess increased flocculating properties over those of spherical particles whose diameter equals the smallest dimension of the micaceous particles.

**Dispersion Desirable for Flotation.**—Edser<sup>(3)</sup> and Sulman<sup>(10)</sup> have come to the conclusion that flocculation is the *sine qua non* of flotation. It is not quite clear whether by flocculation was meant the clumping of mineral particles in association with gas bubbles or by themselves, so that it is not quite possible to endorse the statement without further qualification. It goes without saying, of course, that if the minerals to be floated are properly prepared so that their surface is not wetted, they will tend to form complex clumps with air bubbles ("armored bubbles"), but it does not follow that the rest of the pulp is going to flocculate.

Far from considering general flocculation as necessary, it would seem as though reasonably good dispersion is desirable for successful flotation<sup>(2)</sup>, because if it does not obtain, the opportunity to react with the reagents and to adhere to air bubbles is not fully presented to particles that occur within the floccules. The production of a dispersed pulp would then appear as the first requisite in a slimy pulp, and treatment with the proper reagents to bring the selection of certain minerals should come next.

Perfect dispersion is rarely possible in a flotation operation, because of the wetting effects produced by dispersing agents on the minerals that are to be floated. A compromise between perfect dispersion and complete flocculation has therefore to be frequently accepted as satisfactory. The difficulty in obtaining perfect dispersion is perhaps one reason that flotation results are universally poorer in particles finer than 5 microns than on particles ranging from 5 to 100 microns. The use of reagents that disperse the pulp, such as sodium silicate (waterglass), has been found beneficial. These reagents produce cleaner concentrates, and sometimes yield higher recoveries<sup>(15)</sup>.

**Flocculation by Electrolytes.**—Complete flocculation is necessary for thickening<sup>(14b)</sup>. It can be brought about either through the addition of the proper electrolytes (such as lime) or by causing a gelatinous precipitate to form, which entrains the suspended particles. Other things being equal, thick pulps and heating promote flocculation<sup>(11)</sup>.

Ralston<sup>(11)</sup> found that the coagulating power of ions on ore pulps depends upon the charge that they carry, trivalent ions being more effective than divalent ions and the latter than mono-

TABLE 6.—EFFECT OF ADDITIONS OF ACID AND ALKALI ON THE DISPERSION OF A FINELY GROUND GRANITIC PULP

NaOH, lb. per ton of solid	HCl, lb. per ton of solid	pH, on ad- dition to pure dis- tilled water	pH on ad- dition to rock pulp	Condition of pulp
100		12.7	12.6	All flocculated; clear water; flocs all of one color.
25		12.1	11.6	All flocculated; water slightly muddy; flocs all of one color.
16	.....	11.9	11.0	Mostly flocculated; water muddy; upper flocs much lighter; flocculation slow.
10	... ..	11.7	10.6	Fairly flocculated; water muddy; upper flocs much lighter; flocculation slow.
2.5	.... .	11.1	10.0	No flocculation; water very muddy.
0.25	..	10.1	8.8	No flocculation; water very muddy.
		6.3	8.6	No flocculation; water very muddy.
	0.25	3.9	8.4	No flocculation; water very muddy.
	0.5	3.6	8.2	Flocculation very slight; water very muddy; two colors in flocs.
	0.8	3.4	8.0	Some flocculation; water very muddy; two colors in flocs.
	1.0	3.3	7.8	Marked flocculation; water muddy; two colors in flocs.
	2.0	3.0	7.5	Much flocculation; water slightly muddy; one color in flocs.
	5.0	2.6	6.5	All flocculated; water clear; one color in flocs.
	50.0	1.6	1.8	All flocculated; water clear; one color in flocs.
	400.0	0.7	1.2	All flocculated; water clear; one color in flocs.

valent ions. This is in line with the general observation that the coagulating power of ions carrying single, double, and triple charge is of the order of 1:35:35<sup>2</sup>. Ralston's observations, as well as those of most investigators, have indicated that the coagulating (or dispersing) action of hydrogen and hydroxyl ions are exceptionally large for monovalent ions. Table 6 illustrates the effect on the dispersion of a finely ground granitic pulp of additions of hydrochloric acid and sodium hydroxide; Table 7 the effect of additions of salts having cations of valence 1, 2, and 3; and Table 8 the effect of additions of salts having polyvalent anions with monovalent and trivalent cations.

Tables 6, 7, and 8 broadly support Ralston's findings, but in some details they do not agree. In the light of the data presented here, as well as of some others which are omitted for lack of space, it would seem that the flocculating action of each ion is largely a specific characteristic of that ion rather than of the valence of the ion. Thus silver ions act more like copper ions or lead ions than

TABLE 7.—EFFECT OF ADDITIONS OF VARIOUS SALTS ON THE DISPERSION OF A FINELY GROUND GRANITIC PULP

Reagent added, lb. per ton of solids			pH on addition to rock pulp	Character of sediment	Character of supernatant fluid
NaCl	CaCl <sub>2</sub>	Al(NO <sub>3</sub> ) <sub>3</sub>			
5	...		8.8	Dispersed.	Very cloudy.
20	..	..	9.0	Slightly flocculated.	Cloudy.
50	...	..	9.0	Well flocculated.	Slightly cloudy.
500	.	.	9.0	Very well flocculated.	Slightly cloudy.
5000	..		8.8	Very well flocculated.	Clear.
	1.0		8.8	Slightly flocculated (very slow).	Cloudy.
	2.0	.	8.8	Flocculated.	Slightly cloudy.
	3.5	...	8.8	Well flocculated.	Almost clear.
	5.0	.	8.6	Very well flocculated.	Clear.
		1.0	8.4	Dispersed.	Very cloudy.
		1.5	8.2	Slightly flocculated.	Very cloudy.
		2.0	8.2	Well flocculated.	Slightly cloudy.
		5.0	7.8	Very well flocculated.	Almost clear.
		10	6.8	Very well flocculated.	Clear.
		20	6.2	Very well flocculated.	Almost clear.
		40	5.6	Well flocculated.	Slightly cloudy.
		100	4.6	Dispersed.	Very cloudy.
		500	4.0	Dispersed.	Very cloudy.

like alkali-metal ions, and the effect of base-metal ions is different from that of the alkaline-earth metal ions.

TABLE 8.—EFFECT OF ADDITIONS OF VARIOUS SALTS ON THE DISPERSION OF A FINELY GROUND GRANITIC PULP

Reagent added, lb. per ton of solids			pH on addition to rock pulp	Character of sediment	Character of supernatant fluid
$\text{Na}_2\text{SO}_4$	$\text{Na}_2\text{HPO}_4$	$\text{Al}_2(\text{SO}_4)_3$			
5	.	.	9.0	Dispersed.	Very cloudy.
50	.	.	9.2	Dispersed	Very cloudy.
100	.	.	9.4	Very slightly flocculated.	Cloudy.
250	.	.	9.6	Slightly flocculated.	Cloudy.
500	.	.	9.6	Flocculated.	Slightly cloudy.
	50	.	9.2	Dispersed.	Very cloudy.
	200	.	9.2	Slightly flocculated.	Cloudy.
	500	.	9.2	Flocculated.	Slightly cloudy.
		0.75	8.8	Dispersed.	Very cloudy.
		1.5	8.6	Slightly flocculated.	Very cloudy.
		2.5	8.2	Slightly flocculated.	Cloudy.
		5	7.4	Well flocculated.	Slightly cloudy.
		20	6.2	Well flocculated.	Clear
		100	4.2	Very well flocculated.	Almost clear.
		500	4.0	Well flocculated.	Slightly cloudy.
		2000	3.8	Well flocculated	Cloudy.

**Mutual Precipitation of Colloids.**—It is well known that colloidal solutions are capable of precipitating each other<sup>(7)</sup>. The general explanation is that one colloidal solution is stabilized by the adsorption of positive ions and the other by that of negative ions so that upon mixing, the oppositely charged micelles clump. There is no reason why the same phenomenon should not take place with the colloidal portions of flotation pulps—with harmful results. In this connection some particularly interesting work by Ince<sup>(8)</sup> should be mentioned, in which it was demonstrated that in similar aqueous solutions certain minerals are positively charged, whereas others are negatively charged. It is possible that these minerals occurring in the same pulp discharge each other and result in the formation of complex flocs of an unsuitable character for flotation operations.

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## CHAPTER V

### FLOTATION REAGENTS

Flotation agents or reagents are substances added to the ore pulp prior to or during flotation in order to make possible or facilitate the flotation treatment. The importance of reagents in flotation cannot be overestimated, as without them the application of the process would not be commercially possible in its present form. No other factor approaches reagent control in importance in flotation operations: such vital elements as the determination of adequate pulp grinding or the selection of the best machinery are indeed second to the choice and proper use of reagents.

One of the objects of flotation reagents is to make possible the production of a foam by mechanical means (Chap. VI). If that were the only part played by reagents the metallurgist would be limited to taking advantage of relative native floatabilities (Chap. III). But reagents can modify the native floatability of minerals. This modification of the floatability of minerals, which in turn is a modification of the polarity of the outermost layers of mineral surface, has made possible the magic-like separations of minerals which feature everyday operations.

**Classification of Reagents**<sup>(2)</sup>.—Ever since the early days of flotation, attempts have been made at classifying reagents so that an insight into the proper use of them could be gained. As time went on, the classifications became more complex, and less agreement developed in the meaning of the various terms. This result has come in part because reagents do not necessarily display one function only but often have a manifold use. In spite of the confusion which may exist, it is desirable to discuss reagents largely in terms of their functions.

*Frothing agents* were the first to be recognized as a class by themselves, their function being to create a froth that is capable of bearing non-wetted particles denser than water<sup>(28)</sup>. The frothing function was identified in certain oils which by themselves do not possess any marked tendency to make minerals less wettable by water, but which assist in producing a fragile froth.

*Collecting agents* were the next class of reagents to receive widespread recognition in the days when a substantial amount of oil was still in common use. Certain oils possess the property of gathering certain minerals in a foam, whether or not the oils are the cause for the foam: hence the name of collecting agents. The later term of *promoters*, applied in part to the synthetic chemical compounds that have replaced the collecting oils of "oil-flotation" days, is perhaps better suited to the function of these reagents, but the term *collectors* is so well accepted and unambiguous that there is no need for changing it.

With the development of flotation, a certain class of inorganic salts was recognized as of special action in increasing the flotation of certain otherwise poorly floatable minerals: hence the name of *activating agents* that was given to these substances.

Agreement as to reagent names stops at this point, although many other reagent functions are recognized at the present time. It would seem that these additional reagents have one or several of the following effects:

1. Formation of coatings of a less floatable nature upon the mineral surface. The term *depressing agents* might well be retained for reagents which have this sort of a *positive* inhibiting action.

2. Removal of coatings of a more floatable nature previously formed by activating agents. Reagents that display this *negative* inhibiting action should perhaps be termed *deactivating agents*.

3. Removal of coatings of a less floatable nature previously formed upon the mineral surface. Reagents that display this cleansing action might well be termed *cleansing agents*.

4. pH regulation. *pH regulators* may help or hinder the flotation of certain minerals.

5. Adsorption of micelles of *protective colloids* at selected mineral surfaces.

6. Precipitation by *antitoxic agents*, as insoluble compounds of harmful, naturally occurring salts.

7. Control of dispersion of colloidal portions of flotation pulps by *dispersing agents*.

It is pretty well agreed, now, that reagents may have several functions at one time. For instance, lime may be both a pH regulating agent, a depressing agent for pyrite, and an important factor in dispersion control. Reagents may also have different functions toward different minerals. Thus, sodium cyanide is a

deactivating agent for sphalerite but a cleansing agent for gold tellurides.

### FROTHING AGENTS

**Desirability of Using Frothers.**—The desirability of using some froth-producing agent in flotation circuits is apparent to anyone who has attempted to cause a pure liquid to froth: the result in all cases is the production of a few coarse bubbles which break immediately upon reaching the surface of the liquid. If a pulp is made of pure water and a floatable mineral, the very small load of mineral particles that the coarse air bubbles may be carrying is dropped back in the pulp ("weeping") and no froth results. On the other hand, if a small amount of a frothing agent, such as phenol (say 0.5 lb. per ton ore), is used in addition, the bubbles of gas dispersed in the pulp are smaller, more elastic, and reach the surface without bursting, forming a more or less coherent *froth* or foam.

**Surface Tension and Frothing.**—Liquids foam only if composed of several substances which, if pure, have different surface tensions. From Gibbs' adsorption equation it is seen that the concentration of *A* at the surface of a liquid solution of *A* and *B* is larger or smaller than in the bulk of the solution depending upon the sign of the change in the surface tension of *B* brought about by additions of *A*. Thus, salt solutions have higher surface tensions than water; accordingly the surface of salt solutions presents a deficiency in salt and an excess of water. Similarly, aqueous solutions of alcohol have a lower surface tension than water, and therefore an excess of alcohol in the surface layer. Another conclusion to be derived from Gibbs' equation is that large amounts of a substance raising the surface tension of a liquid (say, water) have to be added to it to produce a material change in surface tension, but that small amounts of a substance lowering the surface tension may be sufficient to bring about a drop in surface tension equivalent to the rise obtained otherwise<sup>(6)(33)</sup>. This conclusion explains (on economic grounds) why all frothing agents used in practice are substances that lower the surface tension of water: they are capable of affecting the surface tension sufficiently even if used in very small amount.

Water has a higher surface tension than nearly all organic liquids but a much lower surface tension than liquid metals. The surface tensions of metals are in the range of 400 to 1200

dynes per centimeter, those of organic compounds in the range of 20 to 60 dynes per centimeter, whereas water has a surface tension of 72.80 dynes per centimeter at 20°C. (74.21 mg. per centimeter if  $g = 981.0$  cm./sec<sup>2</sup>). Almost all organic substances lower the surface tension of water, sometimes amazingly in regard to the amount added. The surface tensions of saturated salt solutions are generally from 5 to 50 per cent higher than that of pure water.

The extent to which substances that lower the surface tension of water affect the surface tension of water (Table 9) is closely related to their structure. The existence of a relationship between the lowering of the surface tension of water by dissolved organic substances and the length of the hydrocarbon chain in the molecules of these organic substances (which in turn determines the solubility of these substances) was pointed out by Traube<sup>(6)</sup>. Broadly speaking, for each CH<sub>2</sub> added to the hydro-

TABLE 9.—RELATIONSHIP BETWEEN LENGTH OF HYDROCARBON CHAIN OF ORGANIC COMPOUNDS AND LOWERING OF THE SURFACE TENSION OF WATER CAUSED BY THEIR ADDITION

Substance	Number of carbon atoms	Approximate amount (parts per million) needed to depress the surface tension of water 5 dynes at 20 ± 2°C.
Acetic acid . . . . .	2	15,000
Propionic acid . . . . .	3	4,000
Iso-butyric acid . . . . .	4	2,000
Iso-valeric acid . . . . .	5	850
Iso-caproic acid . . . . .	6	280
Heptylic acid . . . . .	7	70
Caprylic acid . . . . .	8	20
<i>p</i> -Toluidine <sup>(7)</sup> . . . . .	7	1,650
Xylidine . . . . .	8	460
<i>n</i> -Butyl alcohol . . . . .	4	1,900
Commercial amyl alcohol (pentasol) . . . . .	5	310
Commercial hexyl alcohol . . . . .	6	250
<i>n</i> -Heptyl alcohol . . . . .	7	42
<i>n</i> -Nonyl alcohol . . . . .	9	17
Benzyl alcohol . . . . .	7	2,000
Terpineol . . . . .	10	100
Citronellol . . . . .	10	4
Citronellal . . . . .	10	3

carbon chain the solubility is cut to one-third, and the depression in the surface tension of water resulting from the addition of equimolar amounts of the solute is trebled.

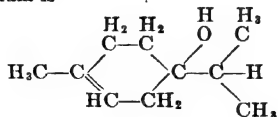
**Characteristic Structure and Composition of Frother Molecules.**—Frothing agents have structural formulas that are characterized by the presence of two constituents having opposite properties<sup>(29)(1)</sup>: one part of the molecule is polar and the other is non-polar, that is one part repels water, while the other hydrates. Typical examples are amyl alcohol ( $C_5H_{11}.OH$ ), cresol ( $CH_3.C_6H_4.OH$ ) and toluidine ( $CH_3.C_6H_4.NH_2$ ).

The frothing properties are related to the composition and structure of both parts of the molecule. Among homologous substances (that is, substances having the same general structure, and therefore the same polar group but varying hydrocarbon chains), the frothing ability at the concentration which yields maximum frothing increases with increase in the length of the hydrocarbon chain, up to a certain point, but decreases if the length of the chain becomes very great. This is particularly well shown in the series of the aliphatic alcohols in which frothing increases with increase in the length of the hydrocarbon chain up to the seven- or eight-carbon-atom alcohol, but decreases thereafter. Substances having the same polar group and about the same solubility, but different structure in the non-polar part of the molecule, have somewhat similar frothing qualities. Thus, hexyl alcohol ( $C_6H_{13}OH$ ) or heptyl alcohol ( $C_7H_{15}OH$ ) is substantially equivalent to terpineol<sup>1</sup> ( $C_{10}H_{17}OH$ ) or xylenol ( $C_2H_5.C_6H_4.OH$ ).

The polar part of the frother molecule is just as important as the non-polar part in determining the value of the reagent. Taggart, Taylor and Ince<sup>(30)</sup> have come to the conclusion that, with few exceptions, all good frothers contain *one polar group, and one only*, preferably a group containing oxygen in the hydroxyl (OH), carboxyl (COOH) or carbonyl (CO) form, or nitrogen in the amine ( $NH_2$ ) or nitrile (CN) form.

**Mechanism of Frothing.**—Frothing can be traced directly to the dual character of frother molecules which have one water-

<sup>1</sup> The structural formula is



avid and one water-repellent portion. Both of these affinities are satisfied if the molecules occur at bubble walls with their polar, hydrated end adhering to the water phase and their non-polar end away from it, so that frother molecules concentrate at the interface between the fluid phases of flotation systems. As a result of the addition of a frother, the gas bubbles formed under the surface of a liquid are more or less completely lined

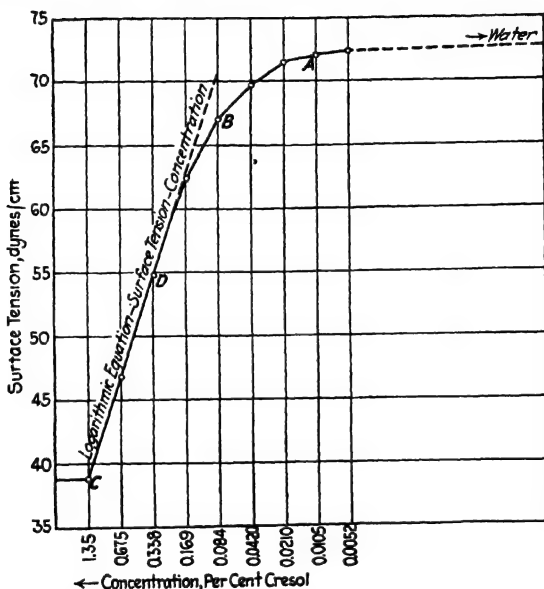


FIG. 4.—Surface tension—concentration curve for concentrated cresol solutions.

with a monomolecular sheath of frother molecules which allows each bubble with its lining to come in contact with other bubbles without coalescing: this forms a froth. In a measure, the effect produced by the addition of a frother is proportional to the amount of frother; past a certain point the effect of further additions of frother is less than that of preceding additions; eventually, the addition of further amounts results in a decrease of the frothing action, and finally in the total absence of frothing<sup>(29)</sup>. The point at which total absence of frothing is obtained corresponds to the saturation by the dissolved substance of the solution.

The peculiar effect of dissolved substances on frothing can be explained as follows. Consider a film of solution  $A + B$  being stretched,  $A$  being the substance of lesser surface tension. As the film is stretched, liquid from the bulk comes to the surface and dilutes it, so that the content of  $A$  in the surface is lessened; accordingly, the surface tension is raised, counteracting the stretching force, and giving the film an elasticity inexistent with pure liquids whose surface tension cannot be increased by a stretching of the surface. Consider now two films made of

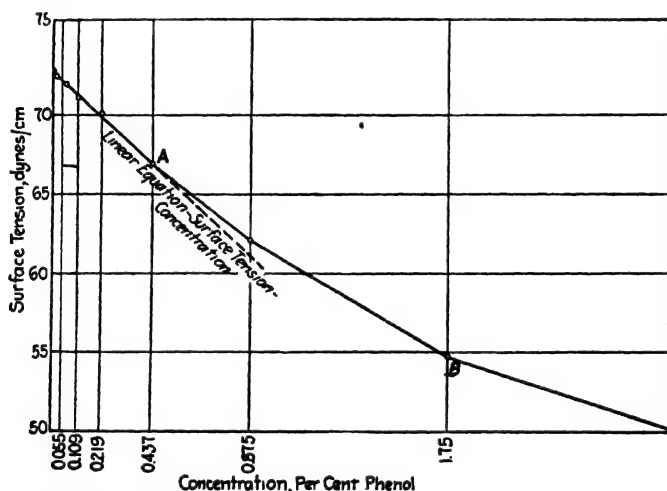


FIG. 5.—Surface tension—concentration curve for dilute phenol solutions.

solutions of  $A$  in  $B$ , the first being more dilute than the second. Upon stretching the films to double their area, the surface tension of each film is increased, that of the film of dilute solution less than the film of concentrated solution, as can be seen by referring to Fig. 5 which shows the relation between surface tension and the logarithm of concentration for aqueous phenol solutions (similar results are obtained with other solutions). Therefore, on the basis of the instantaneous change in surface tension due to stretching, it should be expected that the duration of froths should increase with concentration right on up to saturation. However, the factor of diffusion between the surface and the bulk must not be overlooked. In the case of the dilute solution the ratio of the concentration of  $A$  in the surface to that of  $A$  in the bulk is greater than in the case of the concentrated solution; at the same time the concentration of  $A$



in the bulk is small in the first case and comparatively large in the second. Both of these factors indicate that the attainment of equilibrium is a slower event in the case of the dilute film than in the case of the concentrated film. It would appear, therefore, that the rapid replenishment in the films, of molecules of *A*, in the case of solutions approaching saturation, precludes such films ever having the rise in surface tension that might be expected; also that the resistance of a bubble to rupture might be considered as dependent upon (a) the rise in surface tension resulting from stretching the film, and (b) upon the rate at which the surface-tension-depressing molecules are replenished in the surface by diffusion.

Considerations similar to the above explain why the intermediate homologues of each series of substances are the best frothers: if the higher homologues are used, the dissolved substance will be almost wholly at the surface because of its low solubility (Traube's rule), so that a contraction of surface such as would result from the coalescence of two bubbles will cause local supersaturation, hence disappearance of frothing; if a low homologue is used, the equilibrium between the molecules of solute in the bulk and at the surface will be set up so fast, due to the high concentration of the solute at the surface as well as in the bulk, that there will be no opportunity for a film to increase in surface tension on stretching or to decrease on compression. and therefore the film will present little resistance to rupture.

**Requirements for Frothers.**—The principal quality sought in a frothing agent is found in many substances, but choice is somewhat restricted by certain considerations of which cost, availability, and lack of collecting properties are the most important. The first two are obvious, of course; but the desirability for a lack of collecting properties may not be apparent at first. The reason for placing a premium on that characteristic is that if a substance possesses both frothing and collecting qualities, the intensity of the one cannot be changed with fluctuations in ore character without simultaneous proportionate changes in the other—a very undesirable curtailment in reagent control which is bound to bring decreased mill performance in the treatment of complex ores. Of the various polar radicals, characteristic of good frothing qualities, those which ionize (*e.g.*, the  $-\text{COOH}$  or  $-\text{NH}_2$  group) are also endowed with collecting properties. They are therefore to be avoided in pure frothers.

To sum up, a practical frother must be

1. An organic substance
2. Whose molecules are heteropolar and consist of one or more hydrocarbon radicals attached to one polar group;
3. Whose solubility is neither large nor very small (the range of solubility from 0.2 to 5.0 g. per liter is most desirable);
4. Which does not ionize materially;
5. Which is readily available at reasonable cost.

**Frothers Used in Practice.**—In practice, the most widely used frothers are *pine oil* and *cresylic acid*. Pine oils are of several varieties and include those obtained from the destructive distillation and steam distillation of pine wood, in particular that of pine stumps<sup>(15)</sup>. Of recent years, practice has favored the use of steam-distilled pine oil over that of the destructively distilled oil. The steam-distilled oil contains organic compounds of lower molecular weight and has less collecting power than destructively distilled oil.

Steam-distilled pine oil is composed essentially of terpene hydrocarbons, terpene ketones and terpene alcohols, in particular terpene, pinene, citronellol, and terpineol. Each of these substances has good frothing qualities, but the alcohols (in which OH is the polar group) are better suited for this purpose than the hydrocarbons (in which double bonds act as the polar radical). The terpene alcohols of pine oils are more soluble than the terpene hydrocarbons, produce a froth having very regular cell structure, and have smaller collecting properties. *Terpineol* is available industrially at a reasonable cost and is superior to pine oil as a pure frother. Its use has been recommended by Perkins (*e.g.*, in U. S. Patent 1,364,304) and by others, but no record of its being used in practice can be found, no doubt due to its higher cost.

The *cresylic acid* of commerce is composed of a number of higher homologues of phenol ( $C_6H_5.OH$ ), particularly cresols ( $CH_3.C_6H_4.OH$ ), and xylenols [ $(C_2H_5.C_6H_4.OH)$  or  $(CH_3)_2.C_6H_3.OH$ ]. In most *cresylic acids* of commerce the xylenols are the dominant constituents. *Cresylic acids* are very desirable frothers and their use seems to be spreading at the expense of that of pine oils.

Among the more locally used frothers can be mentioned eucalyptus oil, sagebrush oil, camphor oil, lower aromatic amines, and amyl alcohol. *Eucalyptus oil*, which is obtained from the distillation of parts of eucalypti, has been used for many

years in Australia where the plentiful supply of eucalyptus trees makes it less expensive than pine oil. Eucalyptus oil seems to have somewhat more extensive collecting properties than pine oil as is shown by its use, over a span of years, as the sole organic reagent in the treatment of the Broken Hill ores. *Camphor oil* is used in Japan in place of pine or eucalyptus oil.

*Sagebrush oil* was recommended by Ralston<sup>(3)(22)</sup> in view of the plentiful supply of sagebrush in otherwise waste expanses of the western United States. The lack of an organized sagebrush-oil industry has been one of the factors that have retarded the introduction of this interesting essential oil.

Lower aromatic amines and amyl alcohol have been recommended<sup>(28)</sup> but their use has been restricted on account of cost.

### COLLECTING AGENTS

**Collecting Oils.**—The term *collecting agents* goes back to the days of flotation with oils, at which time it was used to designate certain oils, capable of bringing sulfide minerals in the froth in greater abundance.

According to Taggart, Taylor, and Ince<sup>(30)</sup>, collecting oils gather as droplets at the surface of sulfides, and air bubbles adhere more readily to such oiled sulfides than to unoled sulfides or to gangue. The action of modern collecting agents is apparently very different from the action of the now defunct collecting oils, but the difference is perhaps not as great as might appear at first sight. Let it be assumed that amyl mercaptan ( $C_6H_{11}.SH$ ), which is a very good collector for copper sulfides and copper carbonates, is mixed with kerosene (a mixture of paraffin hydrocarbons) in the proportion of 1 part of mercaptan to 100 parts of kerosene; let it be assumed further that the mixture is used to the extent of 2 lb. per ton, in place of the pure amyl mercaptan (to the extent of 0.02 lb. per ton). The use of the mixed oil results in collection by oiling as defined by Taggart, Taylor, and Ince, whereas the use of the pure mercaptan is of the type commonly referred to as chemical collection. In tests run under these conditions, and with terpineol 0.10 lb. per ton as a frother, on a copper ore from the southwestern United States, the recoveries were 93.6 per cent in the mixed-oil test and 94.2 per cent in the pure-mercaptan test. The similarity in recoveries suggests that the adherence on the floated mineral of oil droplets characteristic of "oil flotation" may be but a secondary effect that

follows the fundamental modification of the surface by the real collector—the mercaptan—just as the adherence of air bubbles to mineral surfaces follows proper preparation of mineral surfaces. In practice, sulfur-bearing crude oils were used to a considerable extent before the advent of chemical collectors, and it is likely that the sulfur compounds in the oils were among the useful constituents. Similarly, the large majority of coal-tar creosotes, wood-tar creosotes, water-gas tars, and other collecting oils contain certain nitrogen compounds of the general group known as “tar bases.”<sup>1</sup> It is likely that in creosotes the nitrogenous compounds (with certain sulfur compounds) are the effective collectors.

**Chemical Collectors.**—*Collecting agents exert their action by adhering to the surface of certain mineral particles, either in their natural state or in some altered chemical form, forming there a non-polar coating that repels water but attaches itself readily to gas bubbles or to non-polar mediums (oil droplets).* The use of collecting agents having different reactivities with different minerals permits of substantial modifications in the relative native floatabilities of minerals listed in Chap. III. This principle is of fundamental importance in selective flotation.

Collecting agents (excluding so-called “collecting oils”) may be classed in two varieties: those that form definite compounds by metathesis with the surface of the minerals, and those that do not seem to do so. The mode of operation of the latter type of collecting agents is not entirely clear, yet it is established that removal of the reagent from solution takes place: it is not known whether the reagent simply adheres to the surface of the minerals or is changed at the surface to a different chemical form.

**Collection by Surface Metathesis.**—The best laboratory demonstration that chemical reaction is responsible for the collection of some minerals is found in the effect of xanthates, particularly the higher xanthates such as amyl xanthate, on copper carbonates, or of thiocresol on lead carbonate. In both cases there is a difference in color between the carbonate and the xanthate or thiocresylate, so that the action is readily visible. Figure 6 illustrates the effect of amyl xanthate on azurite<sup>(8)</sup>. The upper right portion shows the unaltered mineral, and the lower left the coated mineral.

<sup>1</sup> They are called tar bases because they can be extracted from the oils in an aqueous layer through the use of a neutralizing acid (29c).

Treatment of carbonates, phosphates, etc., with soaps of the higher fatty acids, such as sodium oleate, results in an abstraction of the soap by the mineral and flotation of the latter. According to Luyken and Bierbrauer<sup>(17)(18)</sup> a soap is formed by metathesis.



FIG. 6.—Coating produced on azurite by potassium iso-amyl xanthate  $\times 40$ . Two per cent amyl xanthate solution; reaction time, 2 minutes.

**Collection of Sulfides by Xanthates.**—The action of xanthates on base-metal sulfides is by no means thoroughly understood. A few years ago it was postulated that the xanthates adsorbed at the surface of the minerals forming non-Daltonian compounds<sup>(12)</sup>. Subsequently it was shown<sup>(30)</sup> that in the case of galena there is metathesis between oxidized compounds at the surface of the mineral and the dissolved xanthate in the pulp liquor. The inference was drawn<sup>(30)(31)</sup> that the same mechanism accounts for the action of xanthates on other sulfides, but evidence is lacking. Indeed, it is practically certain that the theory of double decomposition between an oxidized coating and the reagent is wrong in the case of pyrite; it may also be incorrect for other sulfides.

The evidence that galena is floated by the formation of coatings of lead xanthate in place of oxidized patches is as follows:

1. Galena oxidizes readily until a thin skin of basic lead sulfate covers it more or less completely.

2. Lead sulfate and basic lead sulfate react with alkali xanthates, forming lead xanthates which are much less soluble than the lead sulfates.

3. Slightly oxidized galena abstracts xanthate ion<sup>1</sup> from solution, and yields sulfate ion in approximately equivalent amount.

4. Slightly oxidized galena treated with an alkali xanthate, then leached with a solvent for lead xanthate, yields lead xanthate.<sup>1</sup>

On the other hand, the evidence that pyrite is not floated by the formation of coatings of iron xanthate in place of oxidized patches is as follows:

1. Ferrous salts form relatively soluble ferrous xanthates. The solubility of ferrous ethyl xanthate, for instance, is about 1 part in 1000, or about a thousand times greater than the concentration of xanthate which is effective in floating pyrite.

2. Ferric salts yield ferrous xanthate and dixanthogen, but no ferric xanthate.

3. Ferrous carbonate (siderite) is not floated by xanthates, up to and including octyl and lauryl xanthates to the extent of 50 lb. per ton.

4. Ferric oxides and hydroxides, and ferrous carbonate, do not abstract xanthate from solution.

5. Badly oxidized pyrite is very difficult to float with xanthates without sulfidizing first.

6. Since pyrite abstracts xanthate ion from solution, and is floated thereby, the action of the xanthate must be other than to form iron xanthate at the surface of the mineral by metathesis with oxidized patches at the mineral's surface.

In one instance an oily compound was extracted from chalcocite which had first been treated with potassium amyl xanthate.<sup>2</sup> This compound was not definitely identified but its properties were suggestive of amyl dixanthogen.

Covellite-plated sphalerite (*q.v.*) abstracts xanthate from solution. This may be the result of oxidation of the covellite coating followed by metathesis between the oxidized coating and the xanthate. But the great solubility of copper sulfate and immediate reaction of copper ions with sphalerite argue against this conclusion.

<sup>1</sup> This result was obtained by M. S. Hansen in the author's laboratory.

<sup>2</sup> HANSEN, M. S., *loc. cit.*

Summarizing the action of xanthates on base-metal sulfides it seems that double decomposition between an oxidized coating and the reagent is the mechanism, at least in part, in the case of galena, that it is not in the case of pyrite, and that it may or may not be in the case of chalcocite and activated sphalerite.

The mechanism by which xanthates float other sulfides than galena may involve the production of dixanthogen, or an adsorption of xanthate ions without further reaction. If an adsorption of xanthate ions on unoxidized sulfide surfaces does proceed, and it appears almost inescapable that it does in the case of pyrite, such an adsorption may well take place even in the case of galena, jointly with metathesis.

**Collection by Organic Sulfides and Disulfides.**—The action of oxidation products of xanthates and hydrosulfides on base-metal sulfides is poorly understood. Organic sulfides, for instance, do not float copper carbonate but they are good collectors for pure chalcocite or pure chalcopyrite. As might be anticipated, badly oxidized copper sulfides are poorly collected by these reagents; it is therefore difficult to visualize their effect on nearly pure sulfides, and yet it is most marked.

For the time being, it is safer to consider that organic sulfides, disulfides, and xanthogens operate by adsorbing upon the surface of the minerals.

**Collection of Activated Silicates by Soaps.**—The case of the flotation of silica and silicates by soaps deserves especial mention. Although early work indicated that fatty acids could be made to float pure quartz<sup>(1)</sup>, subsequent investigation<sup>1</sup> showed this to be due to the activation of the quartz by iron salts derived from the cell walls, through the solvent action of the fatty acids. Warnock's work showed that unactivated quartz is unfloatable and that activation is obtained through the action of all metal ions capable of forming insoluble soaps. Similar activation occurs in the case of a number of silicates preponderantly composed of silica, such as the feldspars. This activation results in an abstraction of metal ions by the mineral, and the activated mineral abstracts soap from solution, so that the general conclusion remains that to be floated by fatty acids or by soaps, minerals must have at their surface a metal oxide which can react with the alkali soap or the fatty acid to form an insoluble soap. Examples of substances that can be floated by soaps and fatty

<sup>1</sup> Unpublished data obtained in the author's laboratory by D. W. Warnock.

acids without activation are bauxite, hematite, calcite, ferberite, apatite, garnet, malachite, and cerussite.

Although the flotation of non-metallics through the use of soaps is to be ascribed to double decomposition if activation by metallic salts is not prerequisite, the same is not necessarily true of the flotation of silica or of that of feldspars which cannot be made to occur in the absence of activation. The activation of silica seems to result from the adsorption of the base-metal ion at the surface of the mineral (perhaps as a colloidal hydroxide), and it is possible that subsequent adsorption of the fatty-acid ion brings about the precipitation, *in situ*, of the insoluble soap which causes flotation of the mineral.

**Collection by Miscellaneous Non-salt-forming Organic Compounds.**—Collection of sphalerite by phenylhydrazine and monoiso-amyl-amine<sup>(10)</sup> and of chalcocite by monoiso-amyl-amine<sup>(14)</sup> and methylquinoline and other tar bases are not explainable at present on the basis of insoluble-compound formation. At the risk of begging the issue it might be well to regard their action as essentially one resulting from an adsorption.

**Characteristic Structure and Composition of Collector Molecules.**—The molecules of collectors, like those of frothers, are composed of two parts endowed with contradictory affinities toward water, one part being polar and the other non-polar<sup>(12)</sup>. Collector molecules differ from frother molecules in that their polar part is capable of reacting with (to form insoluble compounds), or adsorbing at the surface of the minerals to be collected, whereas frother molecules lack this property; accordingly, collector molecules are much more reactive than frother molecules, frequently being ionized to a considerable extent.

As in the case of frothers, increased length of the hydrocarbon chain results in increased effectiveness of the collector; in this case, however, no definite optimum has been established for the number of carbon atoms in the non-polar part of the molecule.

**Selective Collectors.**—The dream of flotation investigators is to find selective collectors, that is collectors that exhibit collection toward one radical, and one only, for instance,  $\text{Cu}^{++}$ ;  $\text{Pb}^{++}$ ;  $\text{CO}_3^-$ ;  $\text{PO}_4^-$ ;  $\text{S}^-$ ;  $\text{Zn}^{++}$ . So far substantial progress has been made, but much remains to be done. For example, soaps collect minerals of all the divalent metals, of all the trivalent metals,



as well as certain compounds of monovalent metals such as silver; lower xanthates collect the copper, lead, iron, silver, and mercury sulfides to the exclusion of zinc, calcium, barium, and aluminum compounds; xanthates collect the lead minerals in preference to copper minerals or mercury minerals; substituted dithiophosphates select the copper minerals; aliphatic mercaptans select the copper, silver, and mercury minerals.

**Collectors Used in Practice.**—A great many substances have been suggested as collecting agents but the number of those that have been found of practical value is remarkably limited. The more widely used collectors include *fatty acids* and *soaps*; *xanthates* and their oxidation products; organic *hydrosulfides* and their oxidation products; substituted dithiophosphoric acids and *dithiophosphates*; substituted *thioureas*; *thiocarbamates*; *azo*- and *diazo compounds*; and higher aromatic *amines*.

**Fatty Acids and Soaps.**—Fatty acids can be considered as derived from hydrocarbons by the substitution of the radical  $\text{—COOH}$  for a hydrogen atom in the hydrocarbon molecule. An example of a fatty acid of the saturated or paraffin series is propionic acid ( $\text{H}_3\text{C.CH}_2\text{COOH}$ ), which can be considered as derived from ethane ( $\text{H}_3\text{C.CH}_3$ ). The fatty acids are among the best known organic compounds, and of the fatty acids those belonging to the saturated series are the most familiar. Every member of the series is known from formic acid ( $\text{H.COOH}$ ) to stearic acid [ $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ]; and their properties vary regularly from one member to the next. Most of the saturated fatty acids occur in nature in one form or another, and particularly as esters (salts of organic acids with alcohols). The lower members of the series are miscible with water, but with increasing length of the hydrocarbon chain the solubility decreases rapidly (after the five-carbon-atom acid, about threefold for each additional  $\text{CH}_2$ ), so that the higher members are substantially insoluble in pure water.

The higher and intermediate fatty acids are practically the only organic compounds found so far to have collecting properties for non-metallic minerals; they have been used with some success in the flotation of oxidized ores, such as oxidized copper ores having siliceous gangues, and in the early days of flotation were used in the flotation of sulfide ores.

By far the most commonly used fatty acid is *oleic acid*. Oleic acid is very similar to stearic acid, but it does not belong to the

saturated series, being a member of the olefine series which is characterized by the presence of one double bond between consecutive carbon atoms. The difference in structure between the fatty acids of the two series is exemplified by ethylene ( $\text{CH}_2=\text{CH}_2$ ) and ethane ( $\text{CH}_3-\text{CH}_3$ ). Oleic acid has enjoyed widespread preference over other fatty acids because of its universal availability, its low cost, and of its being a liquid at room temperature instead of a solid. The latter property is a great advantage in promoting satisfactory and economical reagent addition.

*Palmitic acid* [ $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ ], which is a homologue of stearic acid, has been used in the concentration of African oxidized copper ores, because it is more readily available there than oleic acid.

Other fatty acids which have prospects of being eventually used in the concentration of certain non-metallics, involving delicate selection of minerals of similar floatabilities, are lower in the series than oleic acid or palmitic acid. These fatty acids are scarce in nature, and as there has been no demand for them the price is exorbitant. A substantially unlimited source of supply exists, however, in the saturated and unsaturated hydrocarbons which can be oxidized catalytically to produce a great many useful compounds. It is likely that the catalytic oxidation of hydrocarbons will supply a cheap source of intermediate fatty acids, such as the 7-, 8-, 9-, and 11-carbon-atom saturated fatty acids, known respectively as heptylic, caprylic, pelargonic (nonylic), and undecylic acids.

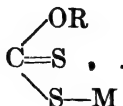
**Xanthates and Their Oxidation Products.**—*Xanthates* which have come to dominate the field of flotation as collectors for sulfides and for oxidized copper and lead ores were discovered by Zeise<sup>(35)</sup> in 1822. They remained a scientific curiosity for nearly 100 years, as their use, in the manufacture of artificial silk, as accelerators for the vulcanization of rubber, and as flotation reagents, has come but in the last 10 or 15 years.

Xanthates are the reaction product of carbon disulfide, an alcohol and an alkali. They are formed by additive reaction in the molecular proportion 1:1:1, with the splitting off of water. The general reaction may be written:



in which R stands for an alkyl hydrocarbon radical and M for a

monovalent (alkali) metal. The structural formula for xanthates is



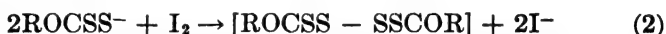
According to L. S. Foster<sup>(5)</sup> xanthates may be prepared as follows:

The alcohol is weighed out into an Erlenmeyer flask and a slight excess over the theoretical amount of saturated potassium hydroxide solution is measured out with a pipette. Then excess carbon disulfide is added, the mixture being cooled in an ice bath, and the whole strongly agitated, mechanical stirring being used if it is available. The precipitate of the xanthate slowly appears and if a great excess of carbon disulfide has not been used the product soon forms into a pasty ball. It is better, however, to add considerable excess carbon disulfide to keep the mixture fluid and to insure better mixing. After 15 min. the excess solvent is removed by means of a water-jet pump, warming the flask in a water bath at 50°C. The product is a yellow, crystalline mass, contaminated with a red-orange liquid, consisting chiefly of an aqueous solution of potassium polysulfides. The latter are removed as completely as possible by pressing with a porcelain spatula on a Buchner funnel. If the product is now dissolved in as small an amount of pure acetone as will take it up, the remaining red watery fluid settles to the bottom and is removed by means of a separatory funnel. On adding petroleum ether to the resulting pale yellow acetone solution, a finely divided, nearly white, flaky precipitate (the pure xanthate) settles.

A great number of xanthates can be prepared, as R (in reaction [1]) can be any member of the alcohol group (except tertiary alcohols), of which several hundred are known, and M any one of four or five alkali metals. Furthermore, by double decomposition with the salts of other metals, a great many more xanthates can be prepared. For practical purposes, few xanthates have been made from alcohols other than those of the paraffin series, and in that series the alcohols higher than the seven-carbon-atom alcohol are so expensive at present that there is little likelihood of their becoming of practical value, unless it is discovered that they have very special qualities, or unless the alcohols from which they are made become much cheaper. Also, xanthates have not been made, so far, from polyalcohols (except cellulose), nor from so-called "tertiary" monoalcohols, that is alcohols in which the OH group is attached to a carbon atom

from which radiate three hydrocarbon chains. The xanthates that can be used in practice include therefore one methyl, one ethyl, two propyl, three butyl, seven amyl, and several hexyl xanthates. Experiment has shown that the various isomeric xanthates have similar effects in most flotation operations, but that there are, nevertheless, some differences between them.

The oxidation products of xanthates include dixanthogens and monoxanthogens. *Dixanthogens* are obtained from the oxidation of xanthates by oxidizing agents such as cupric salts, ferric salts, iodine, or chlorine:



In the laboratory, the preparation of ethyl dixanthogen by means of iodine is particularly easy, and for industrial purposes the preparation by means of a cheaper halogen, such as chlorine, seems to offer great possibilities. Unlike the alkali xanthates, dixanthogens are very little soluble in water. Their insolubility is one of the factors that has mitigated against their general use in sulfide flotation.

*Monoxanthogens* and alkali sulfides result from the breakdown of xanthates. They are particularly pungent, relatively volatile liquids which have given to xanthates a reputation for disagreeable odors. The reaction that yields monoxanthogens is:

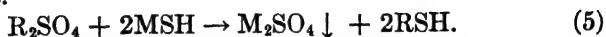


Monoxanthogens are particularly easy to obtain by gentle heating of lead xanthates. Monoxanthogens have substantial collecting power for sulfides but are of little value in the flotation of oxidized minerals.

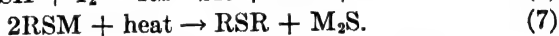
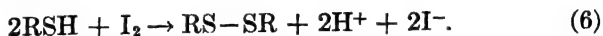
The presence of alkali sulfides, polysulfides, alkalis, and other impurities seems to catalyze the decomposition of xanthates. Moisture also seems detrimental: the presence of impurities in xanthates and consequent deterioration are responsible for the statements that have been made that fresh xanthates are to be preferred to xanthates that have long been standing on the shelf.

**Organic Hydrosulfides and Their Oxidation Products.**—Organic hydrosulfides can be subdivided into a number of classes of which the most important are the mercaptans (or aliphatic hydrosulfides) and the thiophenols (or aromatic hydrosulfides). To this date, little industrial use has been made of these com-

pounds, but their great possibilities as flotation reagents are bending efforts toward cheaper production methods for these substances for which no market has existed heretofore (except perhaps in some instances as rubber accelerators). In the laboratory mercaptans and thiophenols are best prepared by the interaction of alkyl or aryl sulfates with sodium or potassium hydrosulfide.

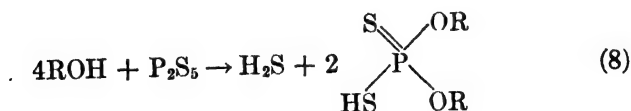


The oxidation products of mercaptans and thiophenols can be made from them either by oxidation with chlorine, iodine, or other convenient oxidizer, which yields the disulfide (a reaction similar to that leading to the production of dixanthogens), or by splitting off  $M_2S$  from a mercaptide or thiocresylate, which yields the sulfide:



**Dithiophosphates.**—Among the more widely used collecting agents for sulfide ores, particularly copper ores, must be mentioned the reaction products of phosphorus pentasulfide ( $P_2S_5$ ) with alcohols and with phenols. These reaction products are strongly acid, and are now marketed either in the acid form or as sodium salts. They were first introduced under the name of "phosphocresylic acid," from the fact that they were made from the cresylic acid of commerce and phosphorus pentasulfide. Later, the name was changed to "aerofloat," and as it was recognized that the reaction product contained a large amount of a dithiophosphoric acid or of a dithiophosphate, their generic name became *dithiophosphates*, under which they will be referred to in this book.

The reaction that yields dithiophosphates is believed to be as follows:



It is best conducted according to the patentee<sup>(34)</sup> at a temperature of about 140°C. in the absence of air.

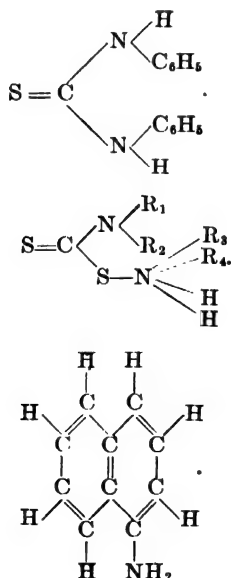
Dithiophosphates are structurally similar to xanthates, the pentavalent phosphorus atom taking the place of the tetravalent carbon atom and binding two alcohol or phenol groups in place of one alcohol group.

**Other Collectors.**—Substituted thioureas, particularly *thiocarbanilid* (diphenyl-thiourea)<sup>1</sup> have been used to a considerable extent. Thiocarbanilid has the distinction of being the first non-frothing chemical collector to be introduced on a commercial scale, but it has been replaced to a large extent by xanthates and dithiophosphates due to the fact that its insolubility in water renders its use difficult. Thiocarbanilid has been used in the pure state or as a 10 to 25 per cent solution in ortho-toluidine. This mixture is marketed under the name of T-T mixture.

Dithiocarbamates,<sup>2</sup> azo and diazo compounds and other nitrogen compounds recommended by Perkins<sup>(21)</sup> have been used experimentally but not on a commercial scale.

*Alpha-naphthylamine*<sup>3</sup> has been used for a long time in one or two plants. Recently, it has been replaced by the more powerful and more easily added xanthates and dithiophosphates. Alpha-naphthylamine is typical of frothing collectors and was introduced in 1917 at the Magma plant in Arizona, one of the first industrial steps toward the elimination of collecting oils.

*Collecting oils* include coal-tar creosotes and coal tar (consisting largely of tar acids and neutral constituents of high molecular weight); wood-tar creosotes which contain, in addition, a number



of tar bases and of terpene compounds; crude oils of high sulfur and nitrogen content and blast-furnace and water-gas oils and tars which are similar to coal-tar creosotes in composition.

### ORGANIC INHIBITORS

Organic inhibitors include two groups of closely related substances one of which is characterized by colloidal properties and is known under the name of protective colloids.

*Protective colloids* (Chap. IV) have been used in a few instances to disperse "secondary" silicate minerals characterized in flotation pulps by fine particle size and ensuing near-colloidal properties. Of secondary silicate minerals sericite and chlorite are particularly frequent sources of difficulty in securing clean concentrates or a good recovery. Gelatin, starch, dextrin, albumen, and glue have been used to a limited extent in this connection.

Non-colloidal organic inhibitors are related to collecting agents in similarity of the polar grouping that attaches to the mineral surface, but they differ in that the other end of the molecule instead of being non-polar is made polar by the insertion of a polar group, such as  $-\text{OH}$  or  $-\text{NH}_2$ . So far, non-colloidal organic inhibitors have not been put to practical use, but they may be in the future. A typical reagent of this class is the reaction product of ethanolamine ( $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ ) with carbon disulfide and alkali (a substance probably similar to a xanthate with an  $-\text{NH}_2$  attached to the end of the hydrocarbon chain). Another example is encountered in dioxyphenylthiourea (whose molecules can be considered to be the same as those of thiocarbanilid, with  $\text{OH}$  substituted for  $\text{H}$  on the non-polar hydrocarbon chains). Of nine organic inhibiting agents not characterized by colloidal properties<sup>(30)</sup> (leucine, malic acid, pyrocatechin, pyrocatechol, thiourea, barbituric acid, gallic acid, glutamic acid, and uric acid), all have several polar groups and six have three or more polar groups. The group that is most typically inhibiting seems to be the  $\text{CONH}$  group characteristic of amino-acids.

### INORGANIC NON-FROTHING NON-COLLECTING AGENTS

**Activating Agents.**—Activating agents are those which through their effect upon the surface of otherwise non-floatable or poorly floatable minerals make them amenable to flotation with the

usual collecting agents. The type example is copper sulfate in connection with sphalerite. Copper sulfate changes the surface of sphalerite to covellite which is readily floated through the use of xanthates or their oxidation products, organic hydrosulfides or their oxidation products, dithiophosphates and substituted thioureas<sup>(9)(10)(23)(24)</sup>. Other salts than copper sulfate act in a like manner on sphalerite. They are discussed in more detail in connection with the flotation of zinc ores.

Activating agents are by no means limited to the treatment of sulfide ores; they play an important part in the treatment or coming treatment of non-metallics. Generally speaking, activating agents are those which are capable of producing less-soluble salts with the collecting agents than any of the metal compounds at the surface of the minerals to be floated. Furthermore, they must be capable of first reacting with the mineral surface, that is, they must form compounds whose solubility is less than that of the metal compounds at the surface of the minerals.

The metals whose organic salts and whose oxides are the least soluble are copper, lead, and mercury. Hence they are also, in salt form, the most effective activating agents.

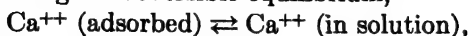
**Sulfidizing Agents.**—Sulfidizing agents, that is agents capable of changing the surface of oxidized minerals of the base metals to sulfide crusts, have been a favorite ingredient in the flotation diet of oxidized ores since 1905<sup>(27)</sup>. In spite of some evidence to the effect that sulfidizing agents are unnecessary<sup>(13)</sup> they continue to be used with some success in the treatment of oxidized ores.

Figure 7 shows the effect of sodium sulfide on cerussite. The left side of the particle shows the unaltered mineral, and the right side the coated mineral.

**Deactivating Agents.**—If activating agents are important in everyday flotation work, the same is true to an even greater degree of deactivating agents. Deactivating agents undo the inopportune work of certain activating agents, which occur naturally in the ore and decrease the difference between the floatabilities of various minerals. One of the best known natural activations that must be undone is that resulting from the action of copper salts on sphalerite in complex lead-zinc or copper-zinc ores. Other examples are the effect of copper salts on pyrite and of calcium salts on quartz. In the first case deactiva-



tion can be brought about by the use of cyanide. • In the case of quartz, it seems that a carbonate, phosphate, or silicate is desirable since each of these reagents forms an insoluble calcium compound and therefore removes the  $\text{Ca}^{++}$  ions from the mineral surface by driving the reversible equilibrium,



to the right.

For a long time, deactivating agents were not identified as such, the belief being that they were simply depressing the



FIG. 7.—Crystalline cerussite sulfidized with sodium sulfide,  $\times 10$ .

Five-tenths per cent sodium sulfide solution; reaction time, 30 seconds. The light-colored area was protected by a paraffin coating which was subsequently removed.

mineral by forming a wettable coating thereon. Recent work has shown that cyanide does not form a coating upon the surface of sphalerite but rather that it dissolves the coating of copper sulfide which has already existed upon its surface.

**Cleansing Agents.**—It has been claimed<sup>(16)</sup> that certain reagents may be used to cleanse floatable surfaces of less floatable crusts, for example that silver sulfides, gold tellurides, metallic gold, silver, or copper, may be cleaned by the use of cyanides. Such a practice is not general although an instance of floating gold in a cyanide circuit has been published<sup>(32)</sup>. The old practice of floating sulfide ores in acid circuits is derived from the desire to cleanse their surfaces of oxidized coatings.

**Depressing Agents.**—In the classification of reagents which is presented here this term is reserved for reagents that form upon mineral surfaces a coating which is less floatable than the natural mineral surface. The use of an alkali chromate in the depression of cerussite may be considered as the type example. The action of the chromate is to form a coating of lead chromate which is much less soluble than lead carbonate and therefore reacts more difficultly with the collector than lead carbonate. Similarly, the action of potassium chromate on partly oxidized galena is one of forming a partial crust of lead chromate which resists reaction with the collector.

It is possible that the effect of cyanide on pyrite is one of coating the mineral surface, but the question should remain open for the time being inasmuch as students of opaque minerals claim that there is no action on pyrite that is manifested by a change in color or by etching even upon treatment with a 20 per cent KCN solution<sup>(4)</sup>. This is in agreement with the findings of Taggart, Taylor, and Ince<sup>(30)</sup> and of S. I. and A. S. Mitrofanoff<sup>(20)</sup>.

It is possible, also, that the effect of lime on pyrite is one of coating the mineral with a reaction product after dissolving the surface of the mineral to some extent<sup>(25)</sup>.

**pH Regulating Agents.**—The use of acid reagents goes back to the early days of oil flotation when acid was used in conjunction with various oils. They were added, in part for the purpose of cleansing the surface of certain sulfides, particularly copper and zinc sulfides, of oxidized coatings.

The addition of alkalis came in at the same time as the use of definite chemical collectors in place of the old-time oils and at the same time as the use of specific reagents to reduce the floatability of certain sulfides while not affecting that of others. Although the reason for their use was not ascertained at the time, it became gradually clear that their use has several objects. Alkaline circuits do not wear the flotation machinery nearly as fast as acid circuits. Also, satisfactory results are obtained in alkaline circuits through the use of a limited amount of collecting agent because alkaline reagents remove soluble salts which otherwise would act as precipitants for collecting agents in solution. The usefulness of alkaline reagents in depressing certain sulfides by affecting the mineral surface through the adsorption of hydroxyl ions, and in affecting the adherence of the collecting agent at the surface of the mineral, has also been recognized<sup>(14)</sup>.

Of the various alkaline substances, *lime* is used to the greatest extent, both because of its specific inhibiting action on the flotation of pyrite which it is generally desired to reject from the concentrate, and because it is far cheaper than the other alkaline substances. *Sodium hydroxide* is not used to a great extent, *soda ash* ( $\text{Na}_2\text{CO}_3$ ) being preferred to it. This may be because lime can be used in place of sodium hydroxide when substantially alkaline circuits are desired, whereas sodium carbonate produces circuits that are nicely buffered in the pH range of 8 to 9.5. Just as sodium carbonate produces circuits that are nicely buffered in the pH range of 8 to 9.5, so *sodium sulfide* produces circuits buffered in the pH range of 8.5 to 10. These two reagents, together with sodium bicarbonate and sodium phosphates, have no doubt been used unknowingly for the purpose of buffering circuits in a certain most desirable range. Their use may also have resulted in a deactivation of certain previously activated minerals.

At present few plants are using acid in their flotation circuits. However, such use seems advisable in the flotation of badly oxidized pyrite, for the production of a clean iron concentrate with a high recovery, and for the inhibition of galena. *Sulfuric acid* is the most widely used acid, because of its availability and low cost.

**Toxic and Antitoxic Agents.**—Under the term of toxic reagents may be grouped certain inorganic salts that have a most profound inhibiting effect on the flotation of minerals. Just what the mechanism of this inhibition is remains unknown; it does not seem to be a case of chemical reaction between the mineral and the toxic substance, such as obtains with depressing reagents that coat the mineral surface, and it is not a case of deactivation, for toxic substances are depressing unactivated minerals. A good example of toxicity is found in the effect of aluminum salts and chromic salts on the flotation of certain sulfides, such as pyrite or galena, or their effect on the flotation of certain oxidized minerals, such as anglesite. The temporary hypothesis may be advanced that the effects of these reagents are to be traced to their hydrolysis to colloidal hydroxides which adhere indiscriminately to the surfaces of most minerals.<sup>1</sup> Under this

<sup>1</sup> Chromic salts are substantially hydrolyzed to chromic hydroxide in solution as acid as pH 2.

assumption it appears that toxic substances resemble protective colloids.

Antitoxic effects are produced by the addition of alkaline salts, perhaps because they result in the precipitation of the colloidal hydroxides in the pulp in the shape of particles of hydroxides or basic salts that are flocculent and less inclined to adhere to mineral surfaces than the dispersed colloidal hydroxides.

**Dispersion Regulators.**—Most of the reagents that affect the pH, likewise affect the dispersion of the colloidal constituents of the pulp. *Sodium silicate* is generally used to disperse fine gangue particles and is very effective as such. It is also slightly alkaline.

To sum up, reagent functions may be classified as in Table 10.

TABLE 10.—REAGENT FUNCTIONS

Reagent functions	Effect on floatability	Seat of action	Polarity	Number of polar radicals per molecule	Ionized	Dissolves a coating from solid	Forms a coating on solid
I. Organic							
1. Frothing	Increases	Gas-liquid interface	Hetero-polar	One	Generally not	No	No
2. Collecting	Increases	Solid surface	Hetero-polar	One	Generally yes	No	Yes
3. Inhibiting (including protective colloids)	Decreases	Solid surface	Hetero-polar	Two or more	Yes	No	Yes
II. Inorganic							
1. Activating	Increases	Solid surface	Polar	Two or more	Yes	Yes or no	Yes
2. Deactivating	Decreases	Solid surface	Polar	Two or more	Yes	Yes	No or yes
3. Depressing	Decreases	Solid surface	Polar	Two or more	Yes	No	Yes
4. Cleansing	Increases	Solid surface	Polar	Two or more	Yes	Yes	No
5. pH regulating	Increases or decreases	In liquid phase and at solid surface	Polar	Two or more	Yes	No	No
6. Gangue dispersing	Increases	Solid surface	Polar	Two or more	Yes	No	No
7. Antitoxic	Increases	In liquid phase	Polar	Two or more	Yes	No	No

## USE OF REAGENTS

It is difficult to give general pointers on the use of flotation reagents, as each type of ore constitutes to a large extent a problem of its own. In Chaps. VIII to XIII are presented numerous data which ought to be of assistance in that connection. The following, however, are general considerations that would appear to apply in most instances.

The variables involved in reagent addition are essentially: (a) the amount of reagent, (b) the place of addition, and (c) the mode of addition.

**Quantity of Reagent.**—Excess or deficiency of any certain reagent is detected by its effect on the pulp, that is, by comparing the froth and pulp appearance either actually or mentally with those of an operation under standard conditions.

Excess of frother is generally marked by the production of an overvoluminous flowing froth which fills launders, and carries a large amount of gangue. This effect is particularly noticeable, by comparison, at the tail end of the flotation operation. Deficiency of frother is marked by a scant froth, and by “weeping” of the mineral from the froth, that is, dropping of the mineral particles by the bubbles at the bottom of the bubble column. The thickness of the froth layer is too great if an excess of frother has been used, and too small if insufficient frother has been used.

Excess of collector results in a dirty froth (particularly if selective flotation is used) as well as in a viscous froth, that overflows difficultly. In respect to froth volume, conditions approximate those obtained if a deficiency of frother prevails. Deficiency of collector yields a thin, poorly mineralized froth and high tailing. It is generally easily detected by vanning the tailing.

Undesirable amounts of other reagents are more difficult to detect and to quantify. It is therefore customary to keep them more nearly constant than the amount of either frother or collector.

**Place of Addition.**—Frothing agents are best added at the flotation cells or just ahead of them. Addition of frothers to the pulp at an earlier stage is of no particular advantage, and it results in undesirable foaming in both classifier and grinding mill.

Collectors may be added to the cells or to the grinding mills or to the classifiers, depending upon the end in view. If collec-

TABLE 11.—REAGENT CONSUMPTION IN THE TREATMENT OF ALL ORES  
IN THE UNITED STATES IN 1929

(Treatment of 65,404,827 tons of ore in 268 plants)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
<b>I. Frothers</b>				
Pine oils ..	215	45,829,007	5,112,776	0.112
Cresylic acid ..	122	26,545,005	4,137,544	0.156
Orthotoluidin ..	5	512,455	32,685	0.064
Total frothers ..	250	64,385,854	9,283,005	0.144
<b>II Collectors</b>				
1. Distillation Products				
Coal-tar creosotes ..	96	10,305,447	1,416,044	0.137
Coal tars ..	3	382,781	30,075	0.079
Wood-tar creosotes ....	10	4,225,775	120,010	0.028
Pine-tar oils ..	1	15,694	3,024	0.193
Petroleum products ..	5	4,230,914	173,502	0.041
Blast-furnace oils ..	8	8,584,122	590,614	0.069
Water-gas tars ..	1	14,912	11,676	0.783
Total ..	99	18,881,674	2,344,945	0.124
2. Synthetic products				
Xanthates:				
Ethyl xanthates .....	221	38,318,235	4,107,056	0.107
Butyl xanthates ..	1	3,609,000	194,252	0.054
Amyl xanthates ..	16	10,952,418	283,270	0.026
Dithiophosphates:				
Dicresyl-dithiophosphoric acid ..	80	13,723,228	610,983	0.045
Sodium dicresyl-dithiophosphates ..	21	11,204,532	208,814	0.019
Sodium diethyl-dithiophosphate ..	2	17,724,100	308,380	0.017
All other dithiophosphates ..	1	37,496	33,320	0.889
Benzyl mercaptan ..	1	31,529	650	0.021
Thiocarbamid ..	14	4,724,980	154,405	0.033
Alpha-naphthylamine ..	12	226,496	23,471	0.104
Total ..	259	65,178,496	5,924,601	0.091
Total collectors ..	268	65,404,827	8,269,546	0.126
<b>III Acids and Alkalis</b>				
1. Acids				
Sulfuric ..	5	540,220	12,099,205	22.030
2. Alkalis				
Sodium carbonate ..	57	10,303,607	4,187,458	0.406
Sodium hydroxide ..	2	99,412	8,338	0.084
Lime ..	99	59,350,561	227,329,427	3.830
Cement ..	2	894,309	3,072,353	3.435
Total alkalis ..	138	62,809,385	234,507,576	3.735
<b>IV. Other Inorganic Reagents</b>				
1. Sulfidizing				
Sodium sulfide ..	19	3,632,048	2,588,676	0.713
2. Activating				
Copper sulfate ..	160	10,726,903	6,723,019	0.627
3. Depressing.				
Cyanides ..	50	25,213,574	1,809,765	0.072
Sodium sulfite ..	9	993,718	813,745	0.810
Sodium silicate ..	20	3,563,972	311,784	0.087
Zinc sulfate ..	41	6,998,687	2,850,775	0.407
Trisodium phosphate ..	2	417,900	18,014	0.043
Total depressing ..	81	27,225,323	5,804,083	0.213
4. Miscellaneous:				
Aluminum sulfate ..	1	2,929,577	15,400	0.005
Calcium chloride ..	1	159,814	92,692	0.580
Sodium chloride ..	2	78,368	103,124	1.316
Sodium sulfate ..	1	2,929,577	20,250	0.007
Sulfur ..	1	454,020	2,115	0.005
Turpentine ..	2	101,566	2,335	0.023
Linseed oil ..	2	44,000	420	0.010
Total reagents ..	268	65,404,827	279,601,530	4.275

tive flotation is desired the collectors may be added at the ball mill or classifier<sup>(26)</sup>. This results in the recovery of many mixed particles containing but a small bulk of the floatable material. For selective flotation, however, it is of advantage to add the collecting agent at the last moment before flotation, or piece-meal during the operation. In the treatment of oxidized minerals, likewise, the collector is advantageously added just before or during flotation.

Other reagents necessitate a variable period of conditioning for reaction with the mineral. This is achieved either by allowing reaction to proceed in a conditioning tank or by adding these reagents ahead of a grinding operation in which case the grinding-mill classifier circuit plays, as well, the rôle of conditioning tank.

**Mode of Addition.**—The ideal way of adding reagents is in solution in water. This, however, is not always possible nor strictly necessary. As a result, some reagents are added directly in the liquid state (frothers, for instance), others are added directly in the solid state (copper sulfate, for instance), others as an aqueous suspension (lime), or as a solution in an organic solvent (T-T mixture).

Two reagents capable of reacting with each other should preferably not be added in concentrated solution too close to each other as this results in waste of reagent and poorer results. For instance, copper sulfate and xanthate should be spaced in their addition to pulps from which sphalerite is to be floated.

**Reagent Consumption.**—The quantity of flotation reagents consumed annually is estimated to be in the vicinity of 200,000 tons. The great bulk of this is made up by lime. Table 11 which is reproduced from the compilation<sup>(19)</sup> issued by the U. S. Bureau of Mines details the reagent consumption in the United States, in 1929.

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## CHAPTER VI

### MECHANICAL ASPECTS OF FROTH PRODUCTION

Froth production can be considered as resulting from three principal steps: gas introduction, gas-mineral attachment, and froth formation. Operative froth characteristics depend largely upon the nature of these steps and upon certain related effects such as the size of bubbles and the pulp consistency. This chapter is devoted to a survey of these aspects of froth production—which may be considered as *mechanical* in contrast with the *chemical* aspects which have been considered heretofore.

#### GAS INTRODUCTION

Following the introduction of gas in an ore pulp previously prepared for flotation the pulp becomes segregated into two layers consisting essentially of water and of gas, respectively; these layers commonly called the *pulp* and the *froth* differ in regard to the relative volume of the gaseous and liquid phases. Both gas-bearing pulp and wet froth are essentially unstable in that creaming and coalescence of the dispersed fluid phase (the gas) is proceeding all the time. Indeed, unless the introduction of air is sufficiently rapid to take care of the coalescence of the bubbles with the surrounding air, no froth forms.

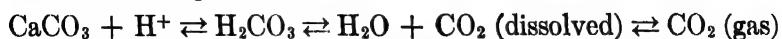
Introduction of gas in a pulp has been accomplished by one of three general methods:

1. *Chemical generation* of bubbles by reaction between an ingredient dissolved in the water and a solid suspended in it.

2. *Evacuation* at reduced pressure, which results in the precipitation of the dissolved gases from solution.

3. *Mechanical introduction* of a gas from outside the pulp.

**Chemical Generation.**—Chemical generation of gas bubbles in a pulp is typified by the Potter-Delprat process<sup>(9a)</sup> in which carbon dioxide bubbles are produced by reaction of sulfuric acid with carbonate particles:



In the operation of the Potter-Delprat process a hot pulp (about 80°C.), a comparatively large amount of acid (2 to 3 per cent by weight, on the water), and a thick, deslimed pulp were found



desirable. Heat decreases the solubility of  $\text{CO}_2$  in water and increases the speed of the gas-generating reaction; a large concentration of acid increases the quantity of gas produced; a thick pulp favors adherence of the bubbles to the collectible minerals; slimes are undesirable because of the too-fast generation of gas and a masking action that results from their presence. It is interesting to note that in the Potter-Delprat process, attach-

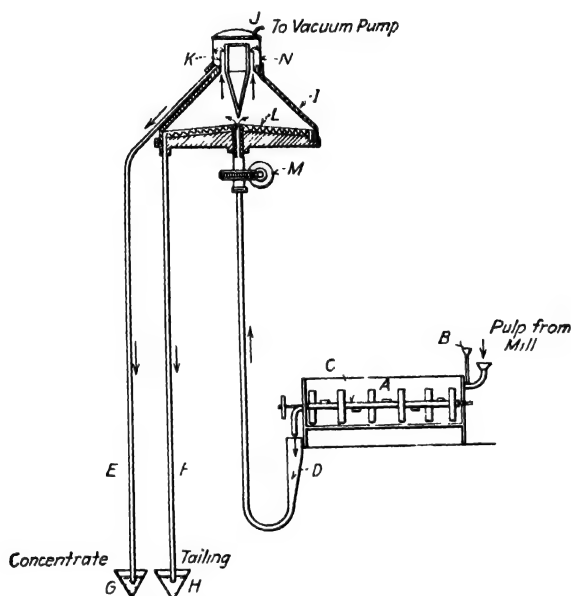


FIG. 8.—Elmore vacuum machine. (After Hoot)

ment of the collected mineral to the bubbles must take place by direct contact of the sulfides with grown bubbles, rather than from gas precipitation on the sulfides, as the bubbles grow at the surface of carbonate particles.

**Vacuum Generation.**—The vacuum processes, which are typified by the Elmore vacuum process<sup>(9)</sup> (Fig. 8) are dependent upon precipitation of the dissolved gases and their adherence to certain suitably prepared mineral surfaces. Vacuum processes are limited in their application by the amount of air that water can hold in solution and therefore eject when subjected to a vacuum.

**Mechanical Introduction.**—Generation of gas bubbles by chemical reaction or by application of a vacuum are obsolete,

as simpler and more flexible methods of mechanical gas introduction have been developed. Mechanical introduction of gas can be achieved by:

1. Drawing gas through a hollow revolving shaft terminating in the pulp by an impeller whose velocity imparts a centrifugal motion to the pulp in which it revolves and therefore sucks the gas (introduction by *sub-aeration*).

2. Drawing air through a vortex formed by an impeller rotating in the pulp (introduction by *agitation*).

3. Blowing gas through pipes dipping in the pulp or through a porous medium submerged in the pulp (*pneumatic* introduction).

4. Allowing the pulp to tumble so as to become mixed with air (*cascade* introduction).

At present, introduction of gas is obtained by one of the first three methods, cascade introduction being substantially abandoned. In spite of this practical consideration it is of interest to view the effects of cascade introduction because of its relation to the other methods. Incipient cascade flotation can be observed by pouring a beakerful of suitably prepared pulp into a partly filled beaker of the same pulp: if the height of fall is sufficient, bubbles appear at the surface of the pulp in the lower beaker and it may be noted that they bring a load of mineral to the surface even if a persistent froth layer does not form. This simple experiment shows that adherence of minerals to air may result from the simple contact of bubbles and particles. It is likely that the same effect proceeds to various extents for sub-aeration, agitation, and pneumatic types of gas introduction.

#### METHOD OF GAS-SOLID ATTACHMENT

**Bubble-particle Encounter.**—The extent to which encounters of bubbles and particles occur is impossible to determine exactly in a complex system such as an aerated pulp. It is, however, capable of analysis for certain much simplified systems for which rather striking results obtain. If it be assumed that a spherical bubble rises with uniform velocity in the direction *OZ* (Fig. 9, 9a) through a perfect liquid, that is one that is incompressible, of no viscosity, and divisible into particles of infinitesimal dimensions, it can be shown<sup>1</sup> that only the particles of liquid located

<sup>1</sup> If it is assumed that water is a perfect liquid, that it is infinitely divisible and that particle and bubble are spherical and moving vertically only, with

along the axis  $OZ$  ever come in contact with the bubble; liquid located originally in the right cylinder having the cross-section of the bubble as its base and  $OZ$  as its axis, but not located exactly on  $OZ$ , are brushed aside as the bubble rises, and crowd past the

uniform velocity, it is possible to arrive at a mathematical estimation of the probability of encounter.

According to R. A. Houstoun ("An Introduction to Mathematical Physics," Longmans, Green and Co., London [1925], p. 25) the velocity potential  $\phi$  of a particle  $P$  of water of infinitesimal dimensions (Fig. 9a) at distance  $r$  from the center of a gas bubble of diameter  $2a$  (with reference to a system of coordinates centered at the center  $O$ , of the bubble) is

$$\phi = \frac{1}{2} V_o a^3 r^{-2} \cos \theta \quad (1)$$

in which  $\theta$  is the angle between the  $Z$  axis and  $OP$ , and  $V_o$  is the velocity of the bubble.

The components of the velocity along  $OP$  and at right angles, in the plane  $ZOP$ , with respect to a system of coordinates, defined as above, is

$$\left. \begin{aligned} u &= \frac{\partial \phi}{\partial r} = V_o a^3 r^{-3} \cos \theta \\ w &= -\frac{1}{r} \frac{\partial \phi}{\partial \theta} = \frac{1}{2} V_o a^3 r^{-3} \sin \theta \end{aligned} \right\} \quad (2)$$

Expressing the velocity of  $P$  with reference to a stationary system of coordinates passing through  $O$ , the velocities are:

$$\left. \begin{aligned} u_1 &= V_o \cos \theta \left( \frac{a^3}{r^3} - 1 \right) \\ w_1 &= V_o \sin \theta \left( \frac{1}{2} \frac{a^3}{r^3} + 1 \right) \end{aligned} \right\} \quad (3)$$

With the signs changed,  $u_1$  and  $w_1$  represent the velocity components of  $O$  with respect to  $P$ .

Repeating the same analysis for a particle  $O'$  falling with respect to  $P$ , the velocities of  $O'$  with respect to  $O$  can be calculated.

The velocity of  $O'$  with respect to  $O$  is the algebraic difference between the velocities of  $O'$  and  $O$  with respect to  $P$  or:

$$\left. \begin{aligned} U &= \left[ V_o \left( \frac{a^3}{r^3} - 1 \right) + V_p \left( \frac{a'^3}{r'^3} - 1 \right) \right] \cos \theta \\ W &= \left[ V_o \left( \frac{1}{2} \frac{a^3}{r^3} + 1 \right) + V_p \left( \frac{1}{2} \frac{a'^3}{r'^3} + 1 \right) \right] \sin \theta \end{aligned} \right\} \quad (4)$$

in which  $V_p$ ,  $a'$ ,  $r'$  relate to the particle symmetrically to  $V_o$ ,  $a$ ,  $r$ .

Choosing  $P$  so that  $\frac{a^3}{r^3} = \frac{a'^3}{r'^3}$  and putting  $R = r + r'$ , and  $A' = a + a'$

$$\left. \begin{aligned} U &= (V_o + V_p) \cos \theta \left[ \frac{A'^3}{R^3} - 1 \right] \\ W &= (V_o + V_p) \sin \theta \left[ \frac{1}{2} \frac{A'^3}{R^3} + 1 \right] \end{aligned} \right\} \quad (5)$$

(Footnote continued on page 90)

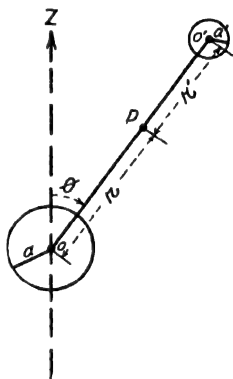


FIG. 9a.

sides of the bubble. A similar result obtains for the settling at uniform velocity of a spherical particle of solid in the liquid, its initial position being considered as that of its center of gravity.

Figure 9 may be considered, as well, as a plot of the paths of a spherical solid particle of center  $O'$  falling with respect to a gas bubble of center  $O$ . The circle  $OMN$  has for radius the sum of the radii of the bubble and particle, so that in order to establish contact between the spherical particle and bubble the path of  $O'$  must touch the circle  $OMN$ . It can be shown that this is not possible unless  $O'$  is vertically above  $O$ . The probability of the particle located in the right cylinder having the bubble cross-section as its base and  $OZ$  as its axis, coming in contact with the bubble is nil, as it is equal to the ratio of the area of a point (cross-section of axis  $OZ$ ) to that of a finite area.

In considering this important result it is well to review the assumptions made in the course of analysis:

1. The water is assumed to be incompressible and to have no viscosity.

By definition distance = velocity  $\times$  time, or

$$\begin{aligned} dR &= Udt \\ R d\theta &= Wdt \end{aligned}$$

Hence

$$\frac{dR}{R d\theta} = \cot \theta \frac{2A^3 - 2R^3}{A^3 + 2R^3}$$

After transposing and integrating:

$$\log \sin \theta + \log R - \frac{1}{2} \log \frac{R^3}{R^3 - A^3} = C$$

or

$$R \sin \theta \left[ \frac{R^3 - A^3}{R^3} \right]^{1/2} = C_2$$

in which  $C$  and  $C_2$  are constants of integration.

Putting

$$\frac{X}{R} = \sin \theta$$

the equation becomes

$$X \left[ \frac{R^3 - A^3}{R^3} \right]^{1/2} = C_2$$

Encounter will take place between bubble and particle if  $C_2$  is nil, that is if  $R \leq A$  or if  $X = 0$ . The condition  $R \leq A$  is not significant since it implies contact or penetration between bubble and particle as a prerequisite to bubble encounter. Hence  $X$  must be nil, meaning that for encounter to take place, bubble and particle must be vertically above each other.

2. The water is assumed to be infinitely divisible.
3. Bubble and particle are assumed to be spherical.
4. Bubble and particle are assumed to be the *only* disturbing factors in an otherwise stationary system.

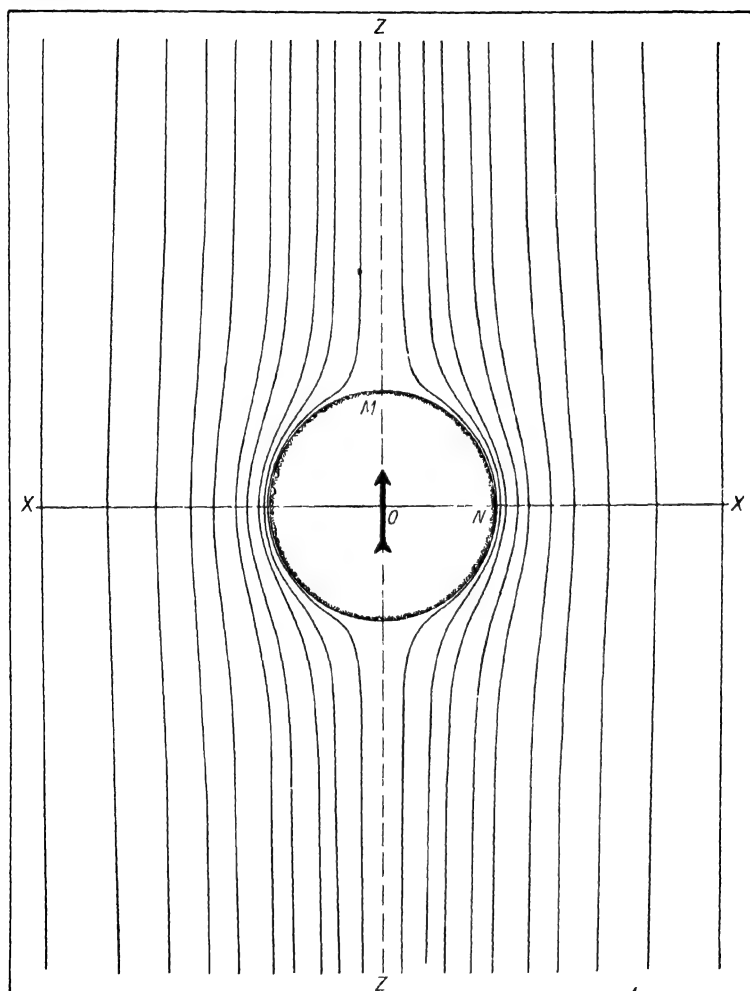


FIG. 9.—Flow-lines of water around a rising bubble.

5. Bubble and particle are assumed to have an irrotational motion.

As a matter of fact each of these assumptions is erroneous except in limiting cases. Consider, for instance, assumptions

3 and 5 together: Solid particles are known to be non-spherical and they, therefore, cannot fall in a liquid, under the influences of gravity and the counter-influence of frictional forces, without presenting complex rotational motions in which volumes of rotation larger than the actual particle volumes are engendered by the particles.

This consideration may perhaps be applied to a crude determination of the variation in the probability of encounter of a non-spherical particle and a bubble with variation in particle size in relation to a bubble of definite size. It leads to the result that if the particle is small compared to the bubble (as in flotation) the probability of encounter between the sphere of rotation of the particle and the bubble varies directly with the size of the particle—otherwise, that if bubble-particle encounters are the basis of gas-solid attachment, the finer the particles the poorer the collection.

The results of these analytical considerations are in agreement with experimental observations as (1) it is very difficult to cause coursing air bubbles to pick up well-prepared mineral particles (it must be stated, in this connection, that the experiment has been tried in relatively thin pulps only); and (2) collection of the very fine particles is not satisfactory either in the laboratory or in practice.

**Method of Gas-solid Attachment in Pneumatic Machines.**—Conditions in machines featuring pneumatic introduction of the gas most closely approximate the experimental conditions realized by allowing coursing air bubbles to rise through a pulp. Yet they differ from them radically in two respects:

1. In pneumatic machines there is a large number of bubbles present simultaneously in the pulp.

2. In the froth ("bubble column") of pneumatic machines there is a still greater proportion of bubbles compared to water and solid, so that a substantially different condition exists there.

Observation indicates that on aerating pulps in pneumatic machines the volume of the pulp (excluding the froth) is distended by 15 to 35 per cent. From this datum it may be estimated that the average distance apart of bubbles in the pulp at their nearest points is of the order of magnitude of the radius of the bubbles. Stated in different terms, the half distance apart of bubbles at their nearest points is of the order of magnitude of one-half the radius of the bubbles. A simple inspection of

Fig. 9 allows the conclusion that bubbles which are such near neighbors affect each others' motion as well as that of the solid particles in the pulp in a manner complex and undeterminable. It should be remarked, furthermore, that all bubbles are not of the same size, so that shearing motions are set up within the pulp due to the differences in velocity of these bubbles; also, that bubbles overtake each other and coalesce.

The bubbles of pneumatically aerated pulps are relatively large (of the order of 0.5 to 1.0 cm. in diameter) and move

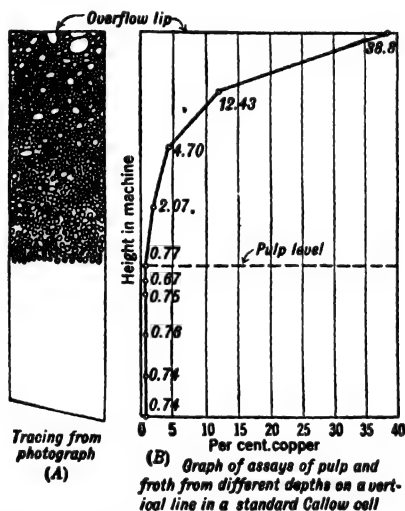


FIG. 10.—Concentrating action in standard Callow cell. (After Taggart.)

rapidly, the time required to rise from the point of introduction to the bottom of the bubble column being of the order of  $\frac{1}{4}$  to 1 sec. under prevailing operating conditions.

The behavior of the bubbles and particles in the bubble column differs from that of a single bubble and a single particle still more than their behavior in the pulp, in that the distance of bubbles from each other is reduced to the vanishing point, in that the bubbles proceed upward with much-reduced velocity, and in that shearing motions between bubbles are accentuated by their relative nearness.

Figure 10, reproduced from Taggart<sup>(12a)</sup>, correlates the assay of the froth or pulp at various heights above the bottom of the cell with the height at which the sample was taken. Figure 10 clearly shows that the metal content at the bottom of the bubble

column is the same as that of the pulp and that the metal content rises gradually from bottom to top of the bubble column. In interpreting the significance of Fig. 10 it must be borne in mind that the assay recorded at every point in the froth is a weighted average of the assay of the bubble wall and of the intervening fluid, in other words that the recorded assay is lower than the true assay of the gas-adhering material by a variable amount which is a function of the relative abundance and composition of the pulp occurring in the froth at that point. The left-hand part

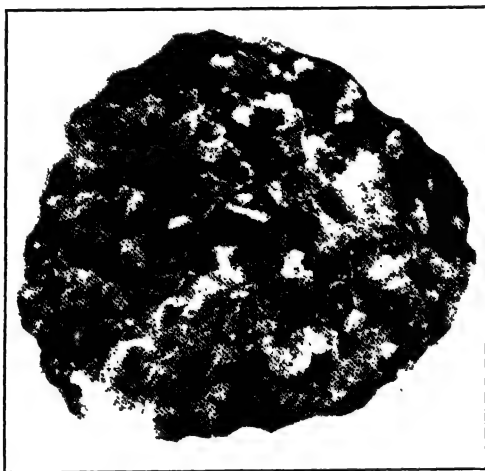


FIG. 11.—Armored bubble,  $\times 25$ .

Produced by agitating biotite (previously treated with a dilute copper sulfate solution) in a very dilute sodium oleate solution.

of Fig. 10 shows that the pulp is gradually eliminated from the bottom to the top of the froth. The conclusion reached by Taggart, in view of the assays recorded in the right-hand part of Fig. 10, that no collection has taken place in the pulp is therefore not necessarily justified. Yet it seems probable that the major part of the collection takes place in the froth. This can be adduced from the fact that the life of every bubble in the froth of pneumatic machines is from five to twenty times that of the same bubbles in the pulp. It follows that, even though there were no improved opportunity for particle-bubble attachment in the bubble column, well over 80 per cent of the attachments should take place there. As a close approximation one may conclude, with Taggart, that in flotation machines featuring



pneumatic introduction of the gas, concentration proceeds essentially in the bubble column.

### Method of Gas-solid Attachment in Agitation-type Machines.

In machines featuring introduction of air by agitation, mineralized air bubbles which may approximate the condition known as "armored" bubbles (Fig. 11) are formed within the pulp and their gathering into a froth may be considered as a simple creaming process (Fig. 12). The bubbles are smaller than in the

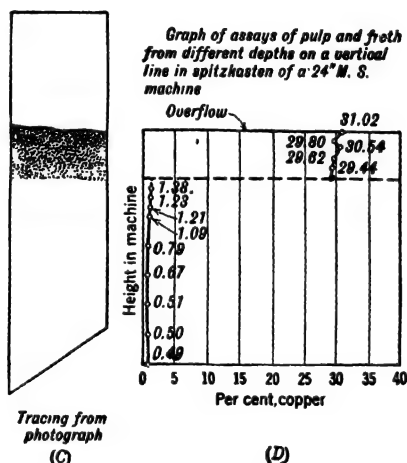


FIG. 12.—Concentrating action in a standard Minerals Separation cell. (After Taggart.)

pneumatic-type machines and their combined volume is less. Indeed, if non-mineralized bubbles were reaching the top of the pulp at the same rate as bubbles reach it in practice in agitation-type machines a very shallow froth only would form.

The mechanism whereby gas bubbles and suitably prepared mineral particles adhere to each other in an agitation-machine pulp to form mineralized bubbles is debatable. Two general modes of attachment suggest themselves: (1) gas precipitation from solution on certain mineral particles, and (2) direct attachment of gas bubbles and mineral particles.

**Gas-precipitation Hypothesis.**—The gas-precipitation hypothesis has been sponsored by Taggart<sup>(12b)</sup> and is based on the following circumstantial evidence:

1. If an aqueous solution becomes supersaturated with respect to a dissolved gas, the gas precipitates selectively at non-polar

surfaces. This may be the basis of the Elmore vacuum process discussed above.

2. A revolving impeller such as is used in agitation-type flotation machines causes a vacuum behind it, which under the conditions of usual operation may range from 5 to 8 in. of mercury. Being saturated with air at atmospheric pressure, the water in the pulp becomes supersaturated at certain specific points behind the impellers, and it is assumed that gas precipitates from solution at those points.

3. A pressure exists in front of the revolving impeller blades, probably of the same order of magnitude as the vacuum in the back of them. At these points solution of gas from bubbles is assumed to proceed.

4. A constant supply of air keeps the pulp saturated. In machines of the M. S. or Hoover type this is achieved by the formation of a vortex.

5. By combining 1 to 4 it may be assumed that gas is precipitated selectively at non-polar surfaces, and thereby causes the formation of highly mineralized bubbles and clusters of bubbles.

**Direct-contact Hypothesis.**—The direct-contact hypothesis is favored by the following considerations:

1. Compared with the bubbles in the pulp of pneumatic machines, the bubbles of agitation machines have a much greater opportunity for direct adherence to particles because of their relatively much longer life in the pulp. This is indicated by the fact that the volume expansion in agitation-type pulps is of the same order of magnitude as in pneumatic-type pulps whereas the volume of air going through a given volume of pulp in a given time may be twenty to one hundred times smaller.

2. As compared with the bubbles in the pulp of pneumatic machines the bubbles of agitation machines are smaller so that more gas-liquid interface is available at any given instant for adherence to solid particles.

3. The mineral particles being coarser in relation to the size of the bubbles, the probability of encounter is increased.

4. In the region immediately about the impeller the relative volume of gas to liquid is substantially greater than in other parts of the pulp, coming nearer to the gas-liquid ratio that obtains in the bubble column of pneumatic machines than that which obtains in other parts of the pulp of agitation machines.

5. The great complexity of the forces at play in the vicinity of the impeller results in considerable shearing and mixing of the pulp as well as in the introduction of special motions of air bubbles and particles which should bring about more frequent encounters.

6. Although some precipitation of air from solution may occur behind the blades of the impellers, it is difficult to see how such an action would be of material importance on account of the nullifying action of the concomitant solution of air that takes place in front of the impeller blades. Also, time would seem to be lacking for growth of precipitated gas bubbles to the size of bubbles produced in agitation machines. Consider, for instance, a four-bladed impeller revolving at 1,800 r.p.m. (an average value for a laboratory machine); the time required for one blade to occupy the position previously occupied by the foregoing blade is  $\frac{60}{4 \times 1,800}$  or  $\frac{1}{120}$  sec.; the pulp, in turning, must have some lag behind the impeller blades, or else motion of the pulp would require no expenditure of work. There are no data available as to what this speed lag is, but it may be variously estimated at from one-half to one-twentieth of the speed of the impeller. Assuming, then, that the pulp revolves at nineteen-twentieths of the speed of the impeller (which gives the gas-precipitation theory the full benefit of the doubt) it follows that the particles of ore on which gas precipitation is to occur pass every  $\frac{1}{6}$  sec. from a condition of gas precipitation to one of gas solution, and back again to one of gas precipitation. On the average, therefore, the conditions that lead to gas precipitation must have a duration of not over  $\frac{1}{12}$  sec., assuming conditions to be as reasonably favorable to gas precipitation as possible. Under these conditions it is difficult to believe that bubbles will grow substantially, since each short period of bubble growth is followed by one of bubble shrinkage. Experimental evidence of the slowness with which bubbles grow is found in the way in which bubbles form under suction at the surface of a submerged non-polarly coated particle: the time required for bubbles to grow to the size of a pinhead is generally of the order of the minute rather than of the second.

7. The very large number of particles carried by a mineralized air bubble makes it necessary to postulate an extensive coagulation of the gas-bearing mineral particles with each other if the

gas-precipitation hypothesis is adhered to. Thus, a fully mineralized bubble 2 mm. in diameter holds some 100,000 particles of average flotation size (10 microns). Its formation, under the gas-precipitation hypothesis could not have resulted without a considerable number of coagulating encounters similar to those postulated under the direct-encounter hypothesis.

Choice between the gas-precipitation and the direct-encounter hypotheses of gas-mineral attachment would seem to depend largely upon the overwhelming evidence that coarse particles (up to a certain size) are floated *much* better than very fine particles (Chap. VII)—a phenomenon that is totally unaccountable by the gas-precipitation hypothesis but that fits in nicely with the bubble-particle-encounter hypothesis.

**Method of Gas-solid Attachment in Sub-aeration Machines.**—Attachment to mineral particles of gas bubbles introduced by sub-aeration partakes of the method of attachment that prevails in both pneumatic and agitation machines. In sub-aeration machines the gas bubbles are of a size intermediate between those found in machines of the other types, the bulk of gas bubbles is larger than in agitation machines but smaller than in pneumatic machines and some heavily mineralized bubbles may be seen to rise to the top of the pulp at the same time as a characteristic weakening of the mineralization of the froth is observed as the top layers of bubbles are brushed back—a phenomenon that obtains also in pneumatic machines.

To sum up, it would appear that adherence of gas bubbles to mineral particles results from the encounter of bubbles and particles, this encounter taking place in the bubble column of pneumatic-type machines, in the pulp near the impeller in agitation machines, and in both the bubble column and the pulp of sub-aeration machines.

**Selection in Gas-solid Attachment.**—It is obvious that the gas-solid attachment pictured as resulting from the encounter of bubbles and particles must be selective between minerals having different surfaces, or else flotation as a concentrating process would be impossible. In the light of the foregoing chapters the importance of the polarity of the surfaces of the minerals will be apparent. If a particle having a non-polar surface encounters an air bubble so that direct adherence of air and solid exists at a certain instant (Fig. 13, left) the contact angles (*q.v.*) that become established at the solid surface indicate

a tendency for the gas to displace the water at the solid's surface. Similarly if a particle having a polar surface encounters an air bubble (which may be difficult because of the hydrated ions residing at the surface of such a particle) the contact angles indicate (Fig. 13, right) a tendency for the water to displace the gas at the solid's surface. Thus, one of the particles will tend to pass in the gas phase and the other to *return* in the aqueous



FIG. 13.—Particle suspension at an air-water interface.

A typical non-polar-surfaced particle and a typical polar-surfaced particle, the latter *temporarily* suspended at a bubble surface.

phase. Return of particles having a polar surface to the aqueous phase is favored by the agitation and subsequent encounters involving the gas bubble and by the crowding effect exerted at the bubble surface by other particles which are better prepared to adhere to the gas.

**Electrostatic Effects and Gas-solid Attachment.**—A few years ago it was thought that electrostatic effects were of great importance in flotation<sup>(2)(7)(4)</sup>, but recent views have largely discredited that view. Briefly, the electrostatic hypothesis of gas-solid attachment is based on the belief that floatable particles and bubbles have at their surfaces electrostatic charges of different sign which cause their coagulation when they chance to pass near each other.

The essential weakness of the hypothesis is that there is no evidence for electrostatic charges occurring under conditions similar to those encountered in flotation. The existence of electrostatic charges at the surface of particles dispersed in the body of a continuous phase presupposes that the phase is a non-conductor of electricity. In aqueous solutions of substantial conductivity, such as the pulp solutions encountered in flotation, electrostatic charges (not *ionic charges*, however) are an impossibility.

Air bubbles and oil droplets are charged in pure water<sup>(11)</sup>, but the charge may be ionic rather than electrostatic. Recent determinations by McBain and Williams<sup>(10)</sup> indicate that the number of free electric charges at the surface of gas bubbles and oil droplets in water is very small.

What appears to have been confused with electrostatic phenomena is the existence at the surface of particles of mineral suspended in water of ionic layers, frequently called Helmholtz double layers after the discoverer of the phenomenon. As far as is known today the Helmholtz double layer of ions occurs at the interface between particles suspended in an electrolyte, and the electrolyte. It consists of a layer of ions bound to the particle surface, surrounded by a second layer less tenaciously held to the surface of the particle. The two layers are of opposite sign. The particle with its ionic layers is therefore substantially neutral if viewed from a distance, but at a close range it may appear charged because of the difference in the distribution of the charges in the two ionic layers. It is likely that the charge on air bubbles and oil droplets is of a character similar to that of the charges on solid particles.

#### STRUCTURE AND SIZE OF MINERALIZED BUBBLES

**Structure of Bubbles.**—The structure of mineralized bubbles may be studied by allowing some bubbles lined with a fairly coarse mineral to dry, then breaking open the dry bubble skeletons and examining them from the inside as well as from the outside. A study of this kind was made with bubbles mineralized with galena, cerussite, malachite, and mica. Figure 14 represents a malachite bubble broken in two and photographed by focussing first on the visible edge, then on the bottom of the shell. Figure 14 shows that the particles line the bubble one deep and that the inside of the shell is relatively smooth. Figure 15, which was drawn from a bubble similar to that shown in Fig. 14, shows also that the particles adhere to the bubble wall with the largest area that is compatible under the circumstances. This is in agreement with the requirement of the second law of thermodynamics dealing with the tendency of surface energy to be a minimum (Chap. V, Frothing Agents).

**Size of Bubbles.**—Considerable interest has attached in the past to the production of air bubbles of the most effective size. Assuming, for the time being, that bubbles of any size can be produced, arguments can be advanced to show the desirability of having large bubbles or fine bubbles. Thus:

1. A given volume of air will have more surface if *finely* dispersed; therefore the amount of solid particles that can be

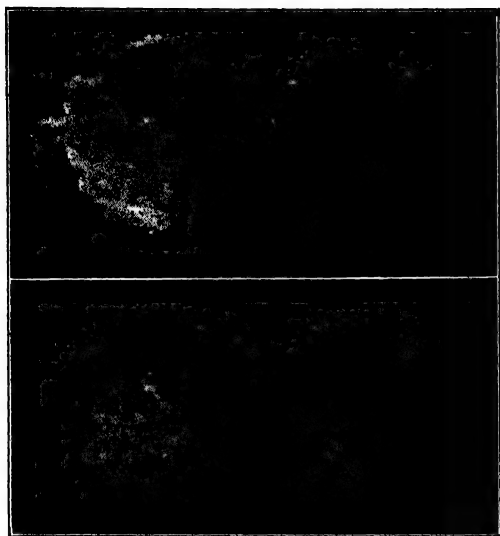


FIG. 14.—Dry mineral-lined bubble,  $\times 20$ .  
Above: focusing on edge; below: focusing on bottom.

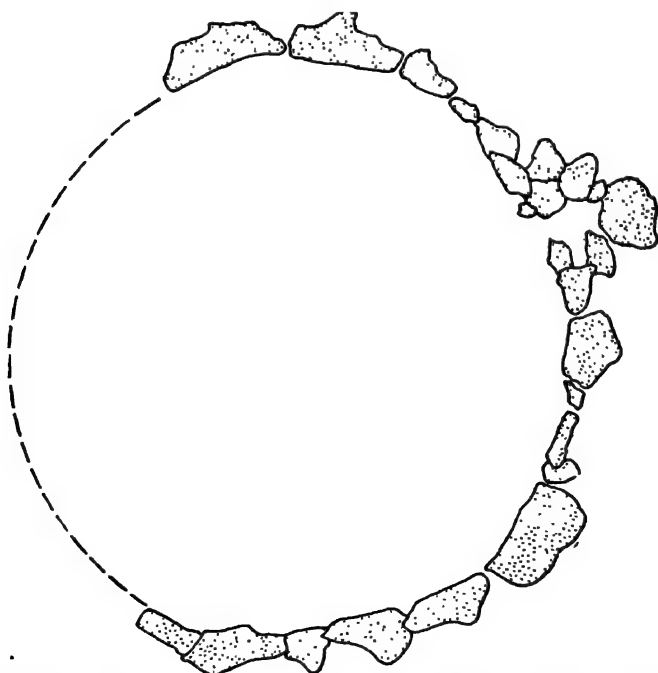


FIG. 15.—Camera-lucida drawing of a dry bubble (section),  $\times 80$ .

accommodated at its surface as a layer one particle deep is greater.

2. It costs energy to disperse gas, and the finer the dispersion the greater the cost per unit volume of gas. It is likely that past

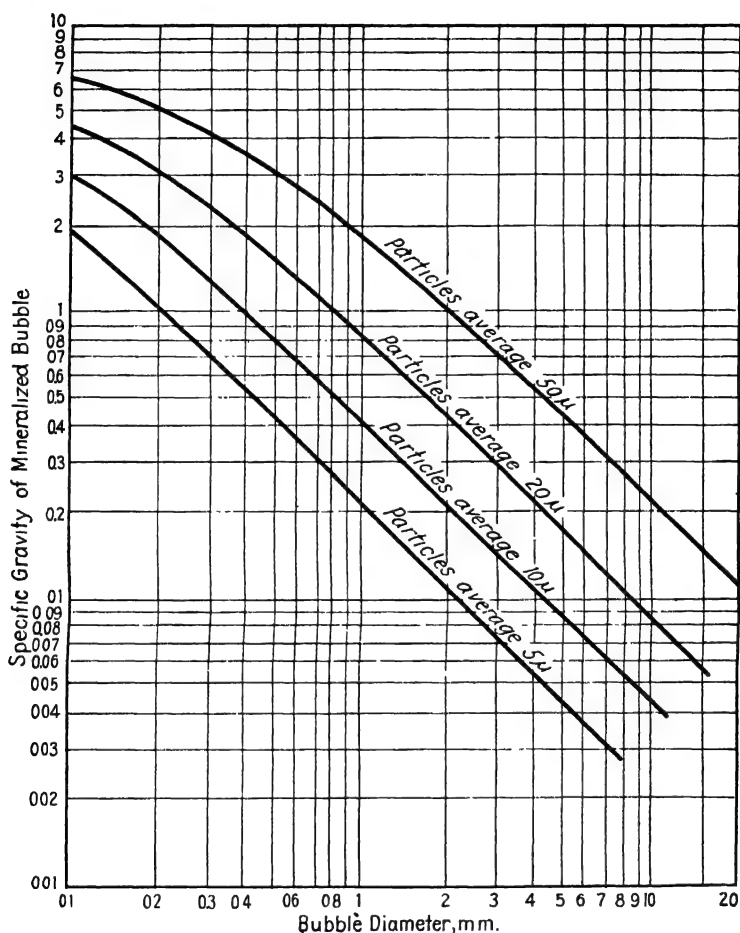


FIG. 16.—Relation between specific gravity of mineralized bubble, size of bubble, and size of the mineral particles.

a certain stage of dispersion of gas in water, the cost of dispersion increases faster than the gas-liquid surface that is produced by it.

3. Of fully loaded bubbles, that is bubbles covered with particles one layer deep, those having smaller diameters have a greater apparent specific gravity, as may be deduced from the



fact that the buoyancy due to the gas varies as the cube of the diameter, whereas the buoyancy-consuming load of mineral varies as the square of the diameter. Bubbles may conceivably

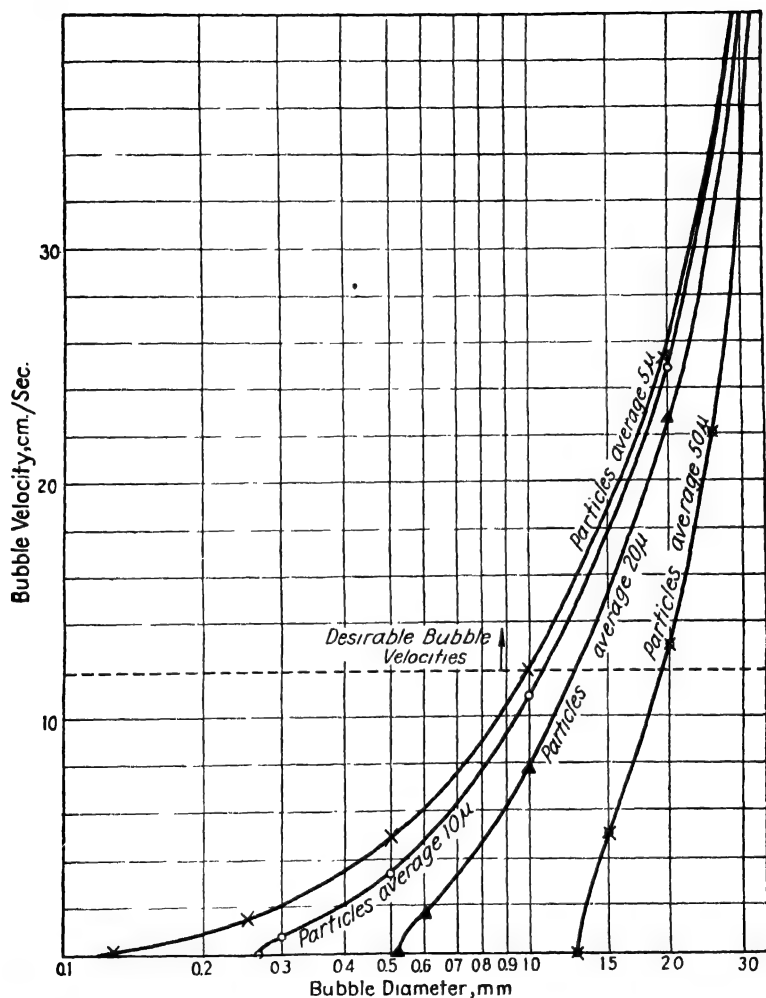


FIG. 17.—Relation between the diameter of a mineralized bubble and the ascending velocity of the bubble in water.

be small enough so as to have the same specific gravity as the surrounding pulp and therefore no tendency to rise with their mineral load. Such a situation is particularly likely to arise in

mechanically agitated machines and may be the source of some losses.

4. Finer bubbles have a better opportunity to become attached to mineral particles and therefore are likely to result in a slightly higher recovery. This would appear to hold for mechanically agitated pulps as well as for pneumatically aerated pulps.

In conclusion of these considerations it would appear that there are objections to very large and to very fine bubbles, so that bubbles of some intermediate size must correspond to optimum conditions. In order to arrive at some idea of the size limit imposed by argument 3—which has reference to mechanically agitated pulps only—the reader is referred to Fig. 16 which gives in logarithmic coordinates the relation between bubble density, bubble diameter, and particle size (assuming the bubble to be fully loaded with galena); and to Fig. 17 which gives in semilogarithmic coordinates the relation between ascending bubble velocity (in still pulp), bubble diameter, and particle size.

The results embodied in Fig. 16 have been obtained on the assumption that the galena particles lining the spherical bubble form an envelope whose thickness equals the particle diameter. The results embodied in Fig. 17 were obtained from those of Fig. 16 and from Allen's law<sup>(1)</sup> of motion of air bubbles, which is said to apply exactly for air bubbles ranging from 0.13 to 1.1 mm. in diameter. According to Allen the velocity is given by

$$v = K \left[ \frac{\sigma - \rho}{\rho} g \right]^{\frac{2}{3}} \frac{(a - b)}{\left( \frac{\mu}{\rho} \right)^{\frac{1}{3}}}$$

in which  $v$  is the maximum uniform velocity of the bubble,  $K$  is a constant = 0.5,  $\sigma$  is the specific gravity of the bubble,  $g$  the acceleration of gravity,  $a$  the radius of the bubble,  $b$  a constant = 0.0034 cm., and  $\mu$  the viscosity of the medium, all expressed in c.g.s. units. The results presented in Fig. 16 assume, moreover, that the pulp density is 1.5.

From Fig. 16 it is seen that if complete lining of the air bubbles is obtained, the lower limit of size of an air bubble that will buoy galena to the surface varies from 0.13 to 1.3 mm. in diameter as the average galena particle varies from 0.005 to 0.050 mm. in diameter; in other words, the minimum bubble size has to

be some twenty-six times the diameter of the average mineral particle carried. In the case of sphalerite or chalcopyrite, the mineral having a density of 4.1, and the pulp of 1.5, the minimum ratio of bubble size to particle size is 12:1. In the case of calcite, the mineral having a density of 2.7 and the pulp of 1.25, the minimum ratio is 8.5:1. In the case of coal, the mineral having a density of 1.35, and the pulp of 1.1, the minimum ratio is

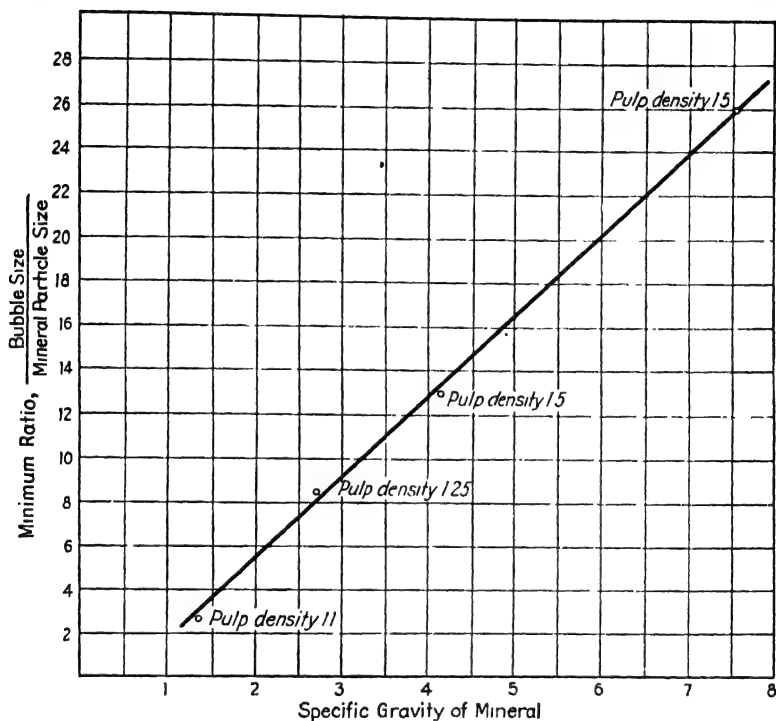


FIG. 18.—Relation between specific gravity of mineral particles and the minimum ratio of bubble size to particle size.

2.5:1. (In the case of coal, approximation to a spherical shell of the film of particles adhering to the bubble is grossly inaccurate; it yields a ratio larger than would otherwise be obtained.) From these data it is apparent that a relation exists between the density of the mineral and the minimum size of bubble that can be used to float the mineral under conditions of high floatability of the particles. Figure 18 summarizes the results obtained and indicates a rough linearity between the ratio of bubble to

particle size and the apparent density of the solid particles in water.

**Minimum Practicable Bubble Size for Creaming.**—To cream readily into a froth, mineralized air bubbles should have a substantial ascending velocity. Mineralized air bubbles should then be larger than mineralized bubbles that are just buoyed by the liquid. In the case of galena, for instance, the ratio of bubble size to particle size should be greater than 26 : 1 (Fig. 18). To have an ascending velocity of 12 cm. per second, which seems to be a convenient lower limit (Fig. 17), a fully loaded bubble carrying galena particles averaging 5 microns in diameter has to be approximately 1.0 mm. in diameter, or two hundred times the size of the mineral particles that it is carrying. For galena particles averaging 50 microns in size, a bubble 1.95 mm. in diameter is sufficiently large to raise the mineral with an ascending velocity of 12 cm. per second. In this instance a bubble only thirty-nine times as large as the mineral particles is sufficient for the purpose. In the cases of sphalerite, calcite, and coal, the minimum bubble sizes are as indicated in Table 12. The differences in bubble size that are required are, of course, in no substantial way responsible for the differences in floatability of these minerals.

TABLE 12.—MINIMUM VELOCITIES OF MINERALIZED BUBBLES NECESSARY FOR A CREAMING VELOCITY OF 12 CM. PER SEC. TO RESULT

I Mineral	II Mineral size, microns	III Pulp density	IV Minimum bubble size for buoy- ancy, mm.	V Minimum bubble size for velocity of 12 cm. per second, mm.	VI Ratio of V to II
Galena	{ 5	1 5	0 13	1.0	200
	{ 50	1 5	1 3	1.95	39
Sphalerite..	{ 5	1 5	0.06	1.2	240
	{ 100	1 5	1.2	2.2	22
Calcite.....	{ 10	1.25	0 085	1 4	140
	{ 200	1.25	1 7	3 3	17
Coal... ..	{ 25	1 1	0 063	1 5	60
	{ 1000	1 1	2.5	4 0	4

The above calculations cannot, of course, give quantitative figures for minimum bubble size that are absolutely dependable because there are a number of factors which it was necessary to

forget temporarily in order to make the problem simple enough to analyze. It would seem permissible, however, to draw as conclusions, the following rules: (1) the coarser the mineral particles, the coarser should be the bubbles; (2) the denser the mineral particles, the coarser should be the bubbles; (3) for average conditions obtaining in practice as to fineness of pulps, the minimum bubble size that is practicable should be in the vicinity of 2 mm. in diameter.

Since coarse bubbles do not carry as much load per unit volume of air as fine bubbles, and since the minimum bubble size that is practicable is in the neighborhood of 2 mm. in diameter, it is not at all striking to find that in practice air bubbles are just larger than the minimum given above.

**Method for Gas Dispersion.**—Fine bubbles can be obtained through two general means, mechanical and chemical. Under mechanical means are included such devices as powerful agitation of air bubbles in water by rapidly moving impellers, and the shearing of large air bubbles into small ones by passage through a constricted space. Under chemical means are included the addition of suitable substances in solution whose object is to make the coalescence of small bubbles into large ones a difficult matter: their use decreases considerably the coalescing of bubbles which would otherwise result from the surface energy relations discussed in Chap. V; thus the effectiveness of the mechanical rupturing of the bubbles is maintained. The best results in dispersing a gas through water are attained through the joint use of mechanical agencies and of frothing agents which, as has already been explained, adsorb at the gas-liquid boundary and by their presence there reduce the tendency of bubbles to coagulate.

### FROTH FORMATION

It has already been indicated that froth formation is essentially a creaming process whereby the light air bubbles with or without attached mineral particles segregate from the heavier pulp. In agitation-type machines the units involved in this creaming are relatively slow-rising, small bubbles heavily loaded with mineral particles. Because of their characteristic mineralization the bubble-mineral aggregates are rigid, and since they reach the top of the pulp at low speed they do not entrain with them

much pulp. In pneumatic-type machines the units involved in the creaming are relatively fast-rising, large, lightly loaded bubbles which on account of their abundance entrain in the bubble column a considerable bulk of pulp.

Changes in the froth as bubbles move vertically upward are twofold: (1) there is a relative downward draining of the water and, to a greater extent, of the suspended solids in the water and, (2) there is more or less pronounced coagulation to larger bubbles. Both of these phenomena are less marked in agitation machines because of the small volume of pulp entrained between the bubbles and because of the relatively finished character of the bubbles.

Since the process of formation of a froth from air bubbles dispersed in a liquid is essentially one of draining the liquid between the bubbles, the draining first proceeds to the point where the walls of adjacent bubbles come in contact at one point, the bubbles retaining a nearly spherical shape; then, as the pulp drains further between the bubbles they assume more and more polygonal outlines (Fig. 19), the angles in the polygonal outlines occurring at places where three bubbles (sometimes more) are in contact. The extent to which air bubbles assume a polygonal outline depends upon (1) the mineralization of the pulp, (2) the size of the bubbles, (3) the size of the mineral particles in the froth. Highly mineralized froths from pulps that are chemically well prepared appear very dry at the surface, and the bubbles are polygonal; poorly mineralized froths obtained in scavenging cells (*q.v.*) and the froths obtained with ores in which the mineral content that is floated is low (as in many precious-metal ores) are composed of spherical bubbles and are high in pulp content. This is to be correlated with the fact that poorly mineralized froths such as form in scavenging machines are shallower than those formed under optimum froth-forming conditions because the lack of mineral particles makes bubble films less persistent. Other things being equal, coarse bubbles or bubbles mineralized by fine particles are more apt to acquire a polygonal shape.

During the draining of pulp from between bubble walls, the drainage of suspended mineral or gangue particles is at first substantially as complete as the drainage of the water except, of course, that of the particles which are suitably prepared to adhere to the bubbles; but, as the bubbles become less spherical in

shape and the particles that adhere to their surface come closer to each other, they exert a sort of filtering action and enmesh a number of gangue particles in the comparatively 'dry' bubble walls. Naturally, the coarser gangue particles are more likely to be retained by the bubble filter of the upper portion of the bubble column. Also, the coarser gangue particles are settling

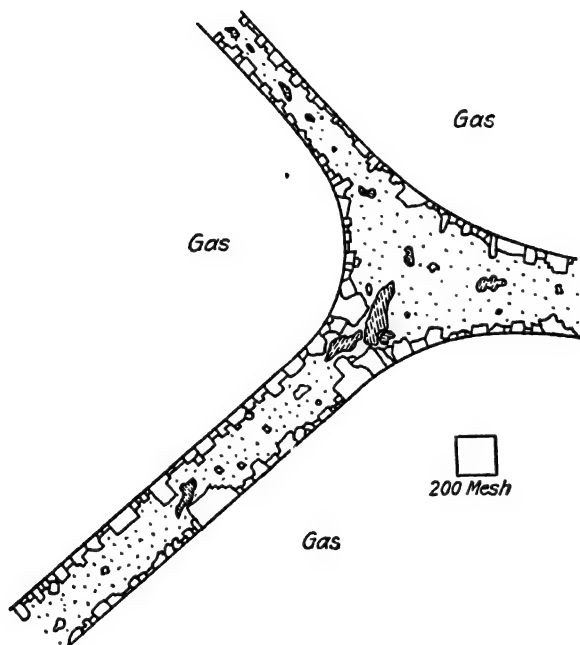


FIG. 19.—Typical appearance of a polygonal froth.  
The white particles represent sulfides; the shaded particles, silicates.

faster in the water so that there is less opportunity for them to find themselves near the top of the froth. These two effects are compensating, so that the unwanted recovery of gangue particles is of the same order of magnitude in the very coarse and in the intermediate size ranges. In the fine size range the gangue and mineral particles alike have such a small descending velocity with respect to the water, that they overflow partly with interbubble water. Also, in spite of their small size, some are large enough to be retained by the bubble filter. As a result, the recovery of fine gangue particles is greater than the

corresponding recovery of the water, and than the recovery of coarse gangue particles.

### FROTH CHARACTERISTICS

Although considerable stabilization of a gas-in-water dispersion is achieved by frothing agents, this stabilization is small when compared with the stabilization which is obtained through the presence, at the boundary between the gas and liquid phases, of dispersed particles of other phases such as oil droplets or mineral particles. An instance is found in the behavior of pine-oil froths. Consider: (1) plain water, (2) a dilute solution of pine oil in water, (3) a dilute solution of pine oil in water containing some soap, (4) a dilute solution of pine oil containing some finely ground graphite. Upon agitation it is observed that there is no foaming with 1, an effervescent (short-lived) foam with 2, and a very much stabler froth with 3 and with 4. Although the stabilizing substances in 3 and 4 are different, the effect is similar. An excellent study of foam stability was made by Bartsch<sup>(3)</sup> who found that the stability of mineralized poly-phase froths is many times as large as the stability of two-phase froths.

In flotation operations a relatively stable froth is desired in order that time be had to remove the froth from the pulp. On the other hand, an overstable, gummy froth is undesirable in that it hinders flow in launders, thickening, and filtering: contrast, for instance, stabilized froths obtained by the help of coarse galena (about 150 microns in diameter), very fine galena (less than 5 microns in diameter), and soap. The soap foam contains no particles that have a substantial settling velocity in water; hence there is no great tendency for the micelles of soap to drain away from the bubble surface; on the contrary, with galena particles having a diameter of about 150 microns, the particles are capable of acquiring a settling velocity in water of 8 cm. per second so that there is a marked tendency for the mineral particles to drain to the bottom part of the bubbles, thus weakening the upper portion of the bubbles which burst. Particles of very fine galena display intermediate properties in this respect, their froths having a permanence intermediate between the permanence of froths stabilized by a coarse mineral and those stabilized by soap.



Froths in which oil droplets coexist with solid particles have a greater persistence than froths that are devoid of them: they resemble froths that contain micelles of soap. This behavior of oil-bearing froths is made possible, even by large oil droplets (of the order of 10 microns in diameter) because of the small difference in density between the oil and the water phases as compared with the density difference between minerals and water. This circumstance explains, in part, the difference in

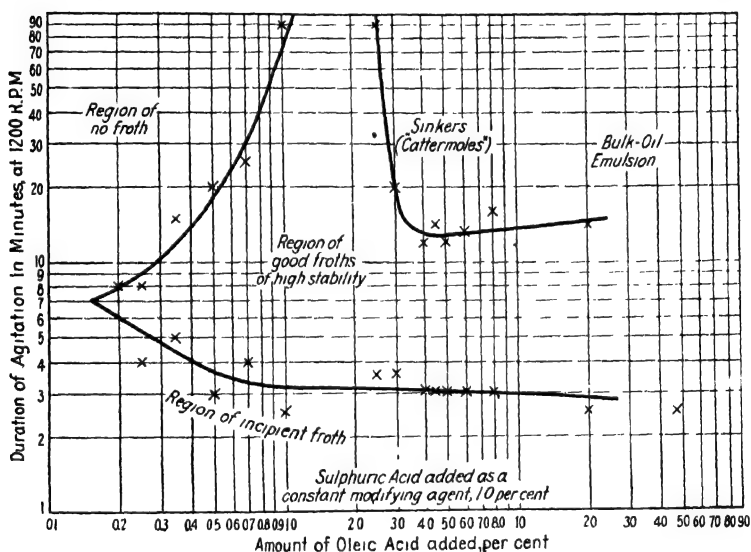


FIG. 20.—Froth flotation and bulk-oil flotation.

Effect of the amount of oleic acid and time of agitation on the character of the froth obtained with a zinc ore.

appearance of the froths obtained through the use of oil in quantity sufficient to form a dispersed oil phase and of the froths obtained through the use of modern chemicals in which there is but one liquid phase. An extreme example of a tenacious polyphase froth is found in whipped cream.

The transition between dispersions involving two liquid phases with various solid phases and dispersions involving one liquid phase and one gaseous phase together with various solid phases is well brought out by a series of experiments which were made in 1925 with a zinc ore (Butte and Superior ore), sulfuric acid (1 per cent), and oleic acid in varying amounts in a Johnson

mixer (an agitating tank, similar in principle to the standard Minerals Separation machines). The results are presented in Fig. 20, whose coordinates are logarithmic plots of the time of agitation and of the amount of oleic acid added. Figure 20 shows that, as the amount of the liquid phase to be dispersed is increased, the froth forms sooner; Fig. 20 shows also that, if comparatively large amounts of oil are used, the froth grades to an oil-solid emulsion containing little air. Froths obtained with a very large or a very small quantity of oleic acid are not nearly as tenacious as those obtained with intermediate amounts of reagent: 1 to 2 per cent yields the most persistent froths. Froths obtained under the optimum stability conditions of Fig. 20 are very persistent. Froths of that character were a continuous source of grief in practice, and retarded the widespread application of flotation.

#### FROTH CHARACTERISTICS DESIRED BY THE OPERATOR

Considerable attention is given by the operator to secure the proper froth texture, mineralization, duration, etc. Unfortunately, up to the present time, it has not been possible to quantify these important factors, which will therefore be discussed qualitatively only.

**Desirable Bubble Mineralization.**—Very low bubble mineralization causes small bubbles to form together with very large bubbles at the top of the froth. This is because lightly mineralized bubbles burst readily at the surface of the pulp. This statement can be verified by comparing the size of bubbles at the feed and tailing ends of a roughing machine.

The use of such a large amount of collecting agent or of such a powerful collector as to give rise to completely mineral-lined bubbles should be avoided, particularly in mechanically agitated pulps, as such bubbles have several undesirable features:

1. Completely mineral-lined bubbles are very rigid and possess little tendency to coagulate. They are, also, substantially smaller and more nearly spherical than the bubbles in froths that are not so heavily mineralized. Because of this circumstance froths of overmineralized bubbles are contaminated by interbubble pulp to a greater extent than froths produced by bubbles whose mineralization is not quite so high.

2. Completely mineral-lined bubbles are inclined to be small and therefore may be denser than the pulp, so that a loss by non-levitation of perfectly good concentrate may take place.

3. The roe-like, leathery froth resulting from overmineralization is difficult to rake over because of its density and because of the tendency of bubbles to roll over each other. In raking the froth some pulp is carried over.

If the amount of collector is suitably adjusted and if the collector is of the proper heteropolar character, the froth will have just enough tendency to coagulate and form polygonal cells so as to be most readily handled. Amyl xanthate, if used on a pulp having a high content of the mineral to be floated, sometimes results in the formation of a roe-like froth, so that its paramount collecting properties are offset by the undesirable physical character of the froth. To overcome this situation some operators have been using a mixture of amyl xanthate with ethyl xanthate. By varying the proportions of the two xanthates with variations in the ore it is possible to keep the froth to the proper texture. The production of an overmineralized froth can also be avoided by gaging carefully the amount of collector and by adding it piecemeal so that no excess reagent is present in the pulp at any time.

Ores that have a small content of the mineral to be floated hardly ever form a roe-like froth, since that condition results from an overmineralization of the gas bubbles; on the other hand the froths obtained with such pulps are frequently undermineralized, watery, and loaded with gangue particles.

**Persistence of Froths.**—Persistence of a froth is dependent principally upon the quantity and quality of the dispersed solid (and liquid) phases in the froth. In modern flotation, the dispersed liquid phase (oil) is almost non-existent, so that the persistence of the froth depends wholly on the quantity and character of the solid in it. The quantity of the dispersed solids adhering to bubble walls can perhaps best be expressed as a percentage of the total bubble surface that is covered by mineral; the quality of the mineral load in terms of the fineness of the solid particles and their shape. Experience shows and reasoning confirms that the greater the percentage of the total bubble area that is covered by mineral the greater the persistence of the froth. This is because the probability of coalescence can be considered as a nearly square function (a square function because

two bubbles are involved) of the relative space at the surface of the bubbles which is vacant of solid and therefore capable of adherence to another similar barren-walled bubble. Experience also indicates that the finer the dispersed solid, the greater the persistence: this is because fine solid particles display almost no tendency to move from their positions on the bubble walls, whereas the same is not true of coarse particles. The shape, finally, is a factor of uncertain character, but it is easy to see how flat particles, for instance, will form a much better envelope than particles of angular shape, and how cubical particles will pack much better than rounded particles.

If it were not for evaporation of the water in the bubble films (to saturate the gas bubbles) it is possible that bubbles fully mineralized with fine solid particles would be substantially everlasting; but water films that have been reduced to a few microns in thickness by draining disappear easily by evaporation. In highly mineralized froths that have just assumed a polygonal shape (interstitial water reduced to a minimum), this results in dried froth skeletons consisting of abutting solid particles.

Overpersistent gummy froths, which do not display the rigidity of overmineralized froths, are obtained when an oil phase is present: this may be because oil droplets can suffer a deformation in shape whereas dispersed solids cannot be deformed but only moved in relation to each other. Froths of this character are difficult to break down even upon addition of water (by means of sprays, etc.) or upon long standing. They lead to pulps that are difficult to thicken and filter.

**Cleaning of Froth.**—Cleaning takes place within the froth by the differential draining of pulp away from the bubbles; it can also be brought about by spraying water upon the surface of the froth. Such a spraying increases the volume of water that is draining through the froth while it dilutes the mineral content of the pulp between the bubbles so that if the froth is equally watery after this treatment as before, it contains less of the unwanted mechanically-carried mineral particles. Also, it breaks the top layer of bubbles, causing them to shower their load on the bubbles below. A crowding effect is produced in which the mineral particles compete for places on the inadequate surface presented, and the result is a heavily mineralized clean froth. The cleaning of froths by refloating them amounts in part to allowing a repetition of the differential draining of

pulp from the froth, and to that extent is in substantial equivalence to spraying a froth during overflow.

**Pneumatic vs. Agitation Machines.**—It has generally been considered that pneumatic flotation machines are better suited for cleaning than for roughing and that the converse is true of agitation machines. This is justified in view of the fact that pulps consisting of rougher concentrates have a relatively higher content of the mineral to be floated, and that when they are aerated in a mechanically agitated machine, there is too ample an opportunity for the formation of completely mineralized bubbles and, therefore, of a leathery, overmineralized froth in which particles are mechanically entrained that ought to be left in the pulp. Highly mineralized pulps, or rougher concentrates that it is desired to clean, are best handled in pneumatic cells in which concentration takes place largely in the froth, so that particles that should be dropped cannot be mechanically carried over into the froth launder. On the contrary, poorly mineralized froths should preferably be handled in agitation cells so as to give the air bubbles an opportunity to come in contact with all of the pulp more thoroughly than is possible in pneumatic machines. The choice of a machine should not be controlled by the consideration of whether the duty is to be roughing or cleaning so much as by the proportion in the pulp of the minerals to be floated.

**Water Content of Froths.**—The water content of the froth, as it is raked into the concentrate launders, is generally in the vicinity of 60 to 80 per cent by weight, being higher the less mineralized the froth is, lower for highly mineralized froths, and least for froths presenting the polygonal-cell structure.

The data presented in Table 13 relate the solid content of the froth, and the relative volumes of the solids adhering to the bubbles and water in the froth to the time period during which the froth was collected from a synthetic galena-granite pulp in a laboratory flotation machine of the mechanically agitated type. The variation in relative volume of the floatable material to water, with time, corresponds to changes in the same variables with place of overflow in continuous plant operations.

In the case of a galena froth containing 50 per cent solids by weight and 60 per cent lead in the solids with the balance a gangue of specific gravity 3.0, the water represents in terms of volume about 84 per cent and the solids 16 per cent, of which

one-half is the volume of the galena and the other half that of the gangue. If it is furthermore assumed that one-quarter of the gangue particles is attached to the bubble walls, it is seen that about 10 per cent of the total solid plus liquid volume is adhering to gas bubbles and 90 per cent is interbubble material. This indicates that the interbubble distance averages about eighteen times the diameter of the particles that are sticking to the bub-

TABLE 13.—CHANGE IN FROTH CHARACTER WITH PERIOD OF FROTH REMOVAL

	Time period of froth removal, min.			
	0-1	1-2	2-4	4-8
Grams in overflow				
Solids . . . . .	102	33	8	6
Liquids. . . . .	48	49	90	407
Galena in overflow				
Percent of total solids by weight. . . . .	96	91	68	43
Ratio, volume of pulp in froth to volume of solids adhering to bubbles. . . . .	3.7	11.8	113	816

bles or, if the sulfide averages 5 microns in size, the average bubble wall has a thickness of the order of 90 microns. According to Hixson, Work, and Odell<sup>(8)</sup>, the average size of particle retained by a filter having an opening of 90 microns is of the order of 15 microns in pulps holding from 20 to 60 per cent solids by weight. Actually, of course, variations in the distance from bubble to bubble exist so that a great many constrictions occur in the size of the apertures of the bubble filter. It is apparent, therefore, that very fine particles only will avoid being caught in the froth. The recovery of extremely fine particles of gangue should be of the same order of magnitude as the recovery of the water, as they overflow with the water on account of their very small settling velocity. This is in agreement with experimental observations.

By a calculation similar to that made above for a froth containing 50 per cent solids it may be determined that if the solid content of the froth is taken as 10 per cent by weight of the combined solids and liquid, the bubble walls average one hundred and fifty times the particle size or about 750 microns, and since

the pulp now has a solid content of only 10 per cent by volume, it is likely that particles as coarse as 100 microns can filter between the bubble walls. This is why considerable cleaning can be achieved by spraying the froth with jets of water, as has already been stated.

**Pulp Dilution and Pulp Consistency.**—Dilution is the ratio of the weight of liquid to that of solids in an ore pulp. Usual flotation dilutions range from 5:1 to 1:1. Pulp consistency is the ratio of the volume of liquid to the volume of solids in an ore pulp. Pulp consistency is always larger than pulp dilution and it is physically more significant although less frequently used. In practice, pulp consistency ranges from 13:1 to 4:1 (see Table 14).

TABLE 14.—PULP CONSISTENCIES IN PRACTICE

Plant	Kind of ore	Density of ore	Pulp consistency
A	Complex lead-zinc ore	4.1	6.8
B	Complex lead-zinc-iron ore	4.3	5.2
C	Collective lead-zinc concentrate	4.6	4.2
D	Disseminated porphyry copper	2.8	8.0
E	Vein copper, high proportion of secondary silicates	3.0	12.1
F	Clean, straight-lead ore	3.0	4.1

From Table 14 it is apparent that the pulp consistency varies within rather narrow limits for similar ores, but that great variations are shown by ores having diverse mineral composition. In general, it seems as though the presence of a hard gangue that breaks to coarse, gritty particles permits the use of a thicker pulp, but that the presence of flaky gangue minerals imposes the use of a thinner pulp.

The subject of proper pulp dilution is one that has not been definitely settled; it is of course to the advantage of the operator to use as high a solid content in the pulp as possible, for this saves water, increases the capacity of the flotation machines (rated in terms of solids passing through each machine per unit time), and causes a saving in reagent consumption particularly in regard to frothers and to reagents that regulate the pH—that is reagents whose seat of action is in the liquid phase or at the

gas-liquid interface. On the other hand, decreased dilution increases the mechanically entrained load of solid in the froth, so that the froth is not as clean as it would be if the pulp were more dilute. This is illustrated by the data of Table 15, from which it may be concluded that the recovery decreases but the gangue rejection increases as the pulp is made thinner. It is noteworthy that the total net loss of metal in the tests presented in Table 15 is nearly independent of the original amount of metal present in the cell, although, of course, the percentage loss is greater in thinner pulps. The practical conclusion to be derived from these considerations is that the pulp dilution should be less for roughing operations but greater for cleaning operations.

TABLE 15.—EFFECT OF PULP DILUTION ON FLOTATION RESULTS

Data obtained with a synthetic mixture of 10 per cent by weight of pure galena and 90 per cent fresh granite, using a constant amount of terpineol (1 drop) and an amount of amyl xanthate proportional to the weight of solid in the cell charge (0.05 lb. per ton)

Charge in cell at start of test, grams		Pulp con- sistency	Concentrate lead, per cent	Tailing lead, per cent	Actual grams of lead lost in tailing
Solids	Water				
2400	2800	3 5	43 4	0 12	2.2
1800	3000	5	56 6	0 14	1.9
1200	3200	8	59 0	0 14	1.4
900	3300	11	62 4	0 14	1 1
600	3400	17	63 9	0 27	1 4
450	3450	23	68 2	0 45	1 8
300	3500	35	74 8	0 56	1 5

Practice in what concerns pulp dilution has varied more in recent years, as it has become dissociated from the natural dilution obtained after classifying through the introduction of thickening between classifying and floating. Further changes in that direction are likely, with advantage to both the classifying operation which requires a comparatively dilute pulp, and flotation which, in certain cases, can be conducted with economy in pulps that are thicker than are practiced today.





## CHAPTER VII

### LIBERATION AND PARTICLE SIZE

**Ores** may be defined as naturally occurring mineral aggregates in which one or more minerals have sufficient economic value to make their exploitation profitable. The net value of an ore depends largely on the gross value of its elemental constituents. It depends also, to an increasing extent, on the form in which the valuable constituents occur, because the valuable content may be more or less expensive to recover, or because its recovery may be more or less complete. Those minerals that enter into the make-up of an ore and are not valuable are known as the *gangue*; the valuable minerals are frequently referred to, by abbreviation, as the *minerals*.

The value of an ore to a smelter depends principally upon its chemical composition, the nature of the compounds making up the ore being of little consequence. In the concentration of ores by flotation, on the other hand, the individual chemical properties of the surfaces of the ground ore particles, rather than the chemical composition of the ore as a whole, are the controlling factors that cause the particles to either float or sink, and determine the value of the ore. To obtain the best results by flotation it is essential to know the mineral make-up of the ore, the character of the surfaces, and the size of the ore particles after grinding. Knowledge of the chemical and physicochemical composition of the soluble and colloidal portions of the ore is also most useful because of the great influence that these factors exert upon the recovery of metal and upon the grade of the concentrate obtained.

An *ultimate analysis*, that is an analysis into constituent elements, is insufficient to determine the possibility of concentrating an ore by flotation. A *proximate analysis*, that is an analysis into the compounds that presumably make up the ore, can be calculated from the ultimate analysis. Proximate analyses give some information as to the mineral make-up of the ore. However, their calculation implies assumptions of mineral occurrence which are frequently in error. No information at

all as to ore structure is given by any kind of chemical analysis; it is, therefore, always desirable to supplement chemical analyses with microscope examinations; it may even be necessary to carry out a careful *microscope analysis*.

### ORE TEXTURE

The microscope examination of polished sections or thin sections discloses the mineral constituents of the ore. It indicates also how the various minerals are associated, and allows a determination of the texture of the ore. By *ore texture* is meant a semiquantitative measure of the size of the grains that make it up. Estimation of the texture of an ore is an important factor in determining the size to which the ore should be ground, in order to liberate its mineral grains into particles consisting of one mineral only.

#### **Effect of Ore Texture on Choice of Concentration Method.—**

Some ores are so coarsely aggregated that crushing to a size coarser than required for flotation results in perfect liberation of the minerals. Such free-milling ores are becoming increasingly scarce because their coarse texture makes concentration by gravity easy, and they, accordingly, have been worked out to a considerable extent. The ready liberation, at a coarse size, in these free-milling ores makes gravity concentration an economically attractive method of beneficiation, in spite of the achievements of flotation; they are, therefore, rarely encountered in flotation work. However, the fine portions of these ores cannot be concentrated by gravity as efficiently as by flotation and are frequently treated in slime flotation plants.

Other ores are so finely textured that crushing to the coarsest size at which flotation is possible does not liberate the minerals. In such cases, even though some liberation results by grinding to 28 or 35 mesh, a substantial proportion of the coarsest particles are true middling particles. Such ores must be ground finer than the coarsest flotation size. Ores requiring fine grinding to unlock the minerals are very numerous, and they supply an increasingly large portion of the world's metal production. A well-known example is furnished by the ore of the Sullivan mine of the Consolidated Mining and Smelting Company of Canada. Hand samples of this ore, which consists largely of

pyrrhotite, pyrite, marmatite, and galena,<sup>(3)</sup> have the appearance of a matte of uniform composition, and the existence of the four minerals is not apparent until the ore is examined under the microscope (Fig. 63).

**Effect of Special Structural Features on the Necessary Fineness of Grinding.**—Some ores that appear at first sight so fine-textured as to require particularly fine grinding fortunately possess redeeming structural features that allow rejection of a substantial portion of waste by relatively coarse grinding. The practice of discarding a clean tailing after comparatively coarse grinding, and of further grinding and floating the concentrate<sup>(7)</sup> should be encouraged because of the resulting economy in grinding. This scheme is used in part at several concentrators and appears at present to be especially applicable to ores featuring secondary enrichment or to ores in which a readily floatable mineral occurs in flaky form, *e.g.*, graphite or molybdenite.

Ores consisting of fine-textured associations of hard and soft minerals, or of brittle and tough minerals, fracture in the course of crushing at the junction of the dissimilar grains. The softness and interstitial character of some sulfides also favor their liberation and their becoming ground to such a fineness as to present enhanced flotative properties. The rôle played by the heterogeneous structural character of ores, as a means for bringing about the unlocking of their minerals with a minimum of crushing, should be emphasized; it would appear possible to make improvements in this direction by the use of more suitable comminuting methods.

**Effect of Extreme Fineness of Texture on Ore Treatment.**—In certain ores some of the minerals are so finely disseminated that extreme comminution is necessary to separate them. The cost of such a comminution might well exceed the profit that could be made by separating the associated minerals, even though this separation by flotation could be made. Just where the economic size limit lies, to which grinding may be carried, depends upon the profit to be made by the separation following liberation, and upon the cost of grinding and separating the associated minerals.

Very intimate mineral associations, which it is uneconomical to segregate under present-day conditions, are exemplified by the occurrence of chalcopyrite, tetrahedrite, and tennantite inclusions in sphalerite. In this connection, L. P. Teas<sup>(15)</sup> says:

Chalcopyrite as minute triangular or rectangular dots, or as stringers, can practically always be found in sphalerite that has been deposited by ascending juvenile waters, the amount varying somewhat directly with temperature and pressure of formation. The dots show a strong tendency to group themselves along crystallographic directions . . . In many cases larger areas of chalcopyrite may be present in the sphalerite in addition to the dots, but this is the exception rather than the rule.

The inclusions described by L. P. Teas result in the gathering of a certain amount of copper and of silver (replacing copper in chalcopyrite, tetrahedrite, or tennantite?) in the zinc concen-

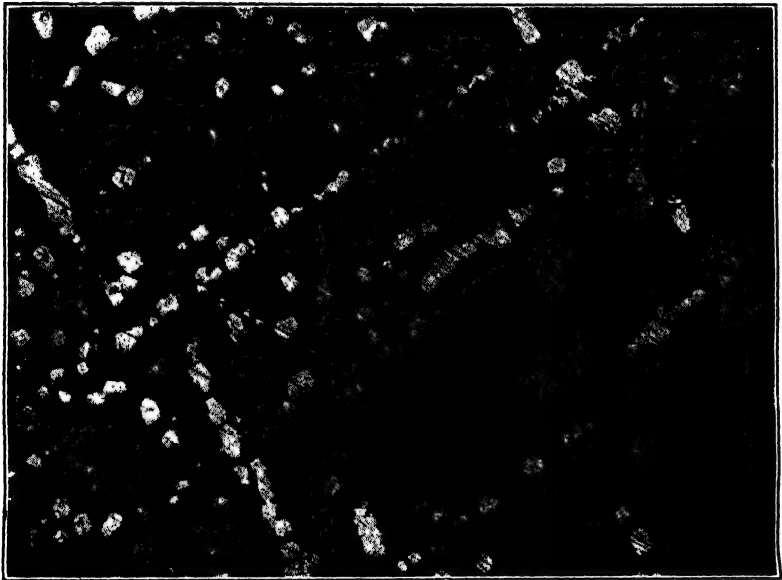


FIG. 21.—Inclusions of chalcopyrite in sphalerite,  $\times 440$ . (*Communicated by P. J. Shenon.*)

The shaded square represents the size of an 800-mesh particle (18.5 microns).

trates of selective flotation plants in which these metals are of less value than in the lead or copper concentrates. The saving from grinding and refloating these copper-bearing and silver-bearing zinc concentrates is, in general, insufficient to pay for the operation because of the extreme fineness of the inclusions. Figure 21 shows that, in one typical instance, grinding to about 5 microns (3000 mesh) would hardly result in unlocking the inclusions.

### EFFECT OF ORE GENESIS

The genesis of ores has an important bearing upon their structure and their flotation. This applies to all kinds of ores, but since flotation is largely applied to ores of igneous origin, the discussion of ore genesis in relation to flotation is limited here to ores of that type.

**Sulfide Ores and Oxidized Ores.**—From the point of view of flotation, ores can be classified into sulfide ores and oxidized ores. *Sulfide ores* are considered to have resulted either from segregation in igneous magmas or by precipitation from hot, ascending, mineral-and-gas-laden solutions. Sulfide ores are necessarily compact as they were formed under high pressure. Although fracturing, dislocation, and faulting accompany their deposition, a porous structure is not obtained. The crystal size of the mineral grains in sulfide ores is relatively coarse. Individual mineral grains are generally composed of a single crystal; sometimes, however, a single crystal of one mineral is much coarser than the average grain size of the ore on account of inclusions of a different composition.

*Oxidized ores* result from the oxidation of sulfide ores, from the leaching away of certain more soluble parts of sulfide ores, or from the precipitation of new constituents brought by downward-percolating solutions. Oxidized ores consist largely of oxides, sulfates, carbonates, and silicates, although chlorides, phosphates, chromates, etc., are found occasionally. Oxidized ores have an earthy instead of a metallic appearance, are characterized by a microcrystalline texture as contrasted with the coarsely crystalline texture of sulfide ores, and are porous instead of compact.

**Effect of Generations of Mineralization on Sulfide-ore Structure and Flotation.**—In a large number of sulfide ores several generations of mineralization are evident, with the result that the structural features of minerals belonging to different generations are different: the oldest minerals are fractured, and cemented by younger minerals which appear under the microscope as veinlets cutting at all angles. In ores of this type the matrix is generally softer and disaggregation takes place readily at the boundary between the grains because of the sudden change in mechanical properties at that boundary. These properties result in the production of comparatively coarse

ore particles derived from the older fractured mineral and of finer ore particles derived from the vein filling. Pyrite frequently occurs as a primary mineral with chalcopyrite and sphalerite fillings. This is shown, by Fig. 22<sup>(10)</sup>, which is a photomicrograph of a sample of United Verde ore. In this sample, the ore appears to consist of pyrite remnants ranging in size from 100 mesh (150 microns) to 1000 mesh (15 microns) cemented by chalcopyrite.



FIG. 22.—Two stages of primary mineralization,  $\times 130$ . (After Lindgren.)  
Pyrite (p) fractured and replaced by chalcopyrite (cp). Gangue appears black (Jerome ores).

**Secondary Enrichment.**—Although similar in some respects to the later stages of primary mineralization, secondary enrichment differs from them in that the sulfide grains have reacted with the metalliferous solution, which may or may not be the case with the later stages of primary mineralization. In other words, secondary enrichment occurs as coatings upon the surfaces

of the primary sulfide grains and may contain the same metal or a different metal from the primary grains. Thus, a worthless sulfide, such as pyrrhotite or pyrite, may be coated with the valuable chalcocite; a valuable sulfide, such as sphalerite, may be coated with a different valuable sulfide, such as argentite or galena; a copper-bearing sulfide, such as chalcopyrite, may be



FIG. 23.—Secondary enrichment. (After Short and Ettlinger.)

Chalcocite replacing pyrite,  $\times 100$ . (Magma Copper Co.) Replacements have followed crystallographic directions (probably octahedral) in pyrite. This type of replacement, although not common, is occasionally encountered in the upper part (supergene part) of the chalcocite zone. It has not been observed in deep-level chalcocite.

coated by another copper-bearing sulfide, such as covellite. The coatings due to secondary enrichment vary considerably in thickness, sometimes completely replacing the substance to the core, sometimes being merely painted over it in a film of minute thickness.

In those cases in which secondary enrichment has reached an advanced stage of replacement of the primary sulfides, the structural character of the ore is very much like that of an ore displaying several stages of primary mineralization as can be seen by



comparing Fig. 23<sup>(11)</sup>, which is a photomicrograph of a sample of Magma Copper Company ore, with Fig. 22.

In those cases in which secondary enrichment has just begun, the coating may be so thin as to be invisible (in section) under the microscope. Due to its thinness the coating may adhere to the primary sulfide more tenaciously than thicker coatings, and thus impart to a large quantity of primary sulfide the prop-



FIG. 24.—Secondary enrichment. (After Lindgren.)  
Sphalerite marginally replaced by argentite,  $\times 130$ .

erties of a small bulk of coating material. Furthermore, even though thin coatings were not more adherent than thick ones, they would bring into the product presumably composed of the coating material a greater proportion of the core substance. It is therefore apparent that from the point of view of the flotation operator, thin coatings of secondary sulfides on a worthless sulfide, or on one that should be collected separately, are just as important as the thick replacements that delight petrographers. An interesting example of secondary enrichment of the "paint" type was encountered at the Eagle mine, Bonanza, Colo., by C. Erb Wuensch<sup>(16)</sup>, who states that "most of the sphalerite . . . has the appearance of the blackjack variety, because of the sooty

coating of secondary argentite." Figure 24(10), illustrates secondary enrichment in the making, representing a somewhat more advanced stage of the same natural process described by Wuensch.

**Secondary Enrichment in Copper Ores.**—Secondary-enrichment phenomena have played a particularly important rôle in the formation of copper ores, possibly because of the extreme insolubility of copper sulfides which, along with mercuric and silver sulfides, are the least soluble of the base-metal and heavy-metal sulfides.

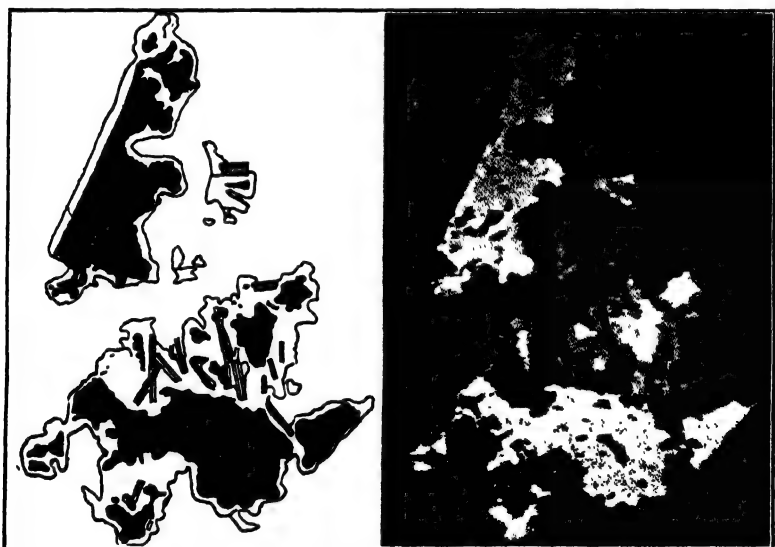


FIG. 25.—Covellite replacing chalcopyrite and bornite,  $\times 96$ . (After Beeson.) Covellite ores (Utah Copper Co., underground). In the sketch (left), black represents chalcopyrite, white, covellite, and the shaded areas, sericite.

In those copper ores in which there is little or no pyrite the enrichment has proceeded upon the surfaces of the primary copper mineral (generally chalcopyrite), and there is no necessity for grinding the ore so as to separate the grain coatings from the core (Fig. 25(1)).

In pyritic copper ores that have been enriched it is necessary to grind to such an extent as to tear the chalcocite, covellite, bornite, or chalcopyrite coatings from the pyrite in order to separate the sulfide copper from the barren pyrite.

Although secondary-enrichment coatings of copper sulfides tend to form on all the sulfides in an ore body, they fortunately

form to a greater extent on nuclei of copper-bearing sulfides. This has been noted by Arthur C. Spencer<sup>(12)</sup>, who, speaking of the disseminated ores at Ely, Nev., says:

Both chalcopyrite and pyrite have been replaced by chalcocite, but the coatings of this secondary mineral are commonly much deeper on the chalcopyrite than on the pyrite, much of which has not been coated at all.

This has been noted also by Beeson<sup>(1)</sup> who states, speaking of the Utah Copper ores, that

polished sections made from ores taken from the upper levels below the capping show the disseminated sulfide grains to be coated with covellite. The coating of covellite is usually much deeper on the chalcopyrite grains than on the pyrite; and when it is found as a coating partly or completely encircling the pyrite grains it is usually possible to see fragments of chalcopyrite in the covellite, indicating that the covellite was formed by the replacement of chalcopyrite rather than pyrite.

Due to the relative thinness of copper-sulfide coatings on pyrite, the amount of copper that would be lost if these coated particles could be dropped during the flotation operation would be small. It is, however, not possible to drop pyrite particles coated with sulfide-copper minerals from a mixture with truly copper-sulfide particles because of the identity of their surfaces. Fine grinding of pyritic copper ores presenting restricted amounts of secondary enrichment, together with the use of suitable reagents to remove the invisible copper-sulfide films from the pyrite particles, is necessary in order to concentrate them by selective flotation.

**Effect of Hydrothermal Gangue Alteration on Constitution of Flotation Pulps.**—The solutions that bring about the deposition of ores, or solutions closely related to them, alter the rocks through which they percolate.

Two general alterations are noticeable: (a) silicification, (b) kaolinization, chloritization, and sericitization. *Silicification* alters sedimentary and igneous rocks alike through the solution of some constituents of the rocks and the deposition of interstitial cementing silica. *Kaolinization* and *sericitization* are processes of alteration which affect feldspars, and are therefore limited to igneous and to some metamorphic rocks. Kaolin

and sericite are hydrous aluminum silicates of more or less definite composition and of cryptocrystalline, fibrous habit: a feldspar crystal in a granite or a diorite is often replaced by millions or even billions of sericite or kaolin grains arranged in fibrous aggregates. *Chloritization* affects ferromagnesian minerals in much the same way as kaolinization and sericitization affect the feldspars.

Because of their microcrystalline habit, sericite, kaolin, and chlorite give rise to an enormous number of very fine particles ranging from 600 mesh to colloidal sizes, even under conditions of moderately coarse grinding. A large proportion of the so-called "primary slime" in ore pulps is derived from these microcrystalline alteration products of primary minerals.

**Oxidized Ores.**—Oxidized ores are more complex than the sulfide ores from which they are derived, because of the mechanism of the transformation. The active ingredients in this alteration are, primarily, oxygen, carbon dioxide, and water, and, secondarily, salts of metals susceptible of acquiring several valences, such as iron sulfates. The complexity of the factors involved, together with the fast-changing concentration of the reacting substances from place to place, makes it possible to find side by side almost all the possible oxidation products.

The new minerals formed in the course of oxidation do not result from the operation of a continuous natural process: there are seasonal changes, in particular, that bring about periods of comparative drought and oxidation, and others of greater humidity and solution. This, together with the low temperature at which the change takes place, gives rise to microcrystalline or even to amorphous oxidation products; it fosters the haphazard precipitation of limonitic coatings and the formation of clayey constituents, which may cover in part the surfaces of the valuable minerals, as well as fill cracks within them. The valuable minerals themselves may be pseudomorphic after the original sulfides, and therefore porous. This is one of the causes of the large consumption of reagents in the flotation of oxidized ores.

**Semioxidized Ores.**—Semioxidized ores are still more complex than oxidized ores because they present the complexities of both sulfide ores and oxidized ores. In a semioxidized lead-silver ore from the Tintic district silver occurred, according to A. W. Hahn<sup>(6)</sup> in at least 13 different forms. Naturally, ores of this character are most difficult to concentrate successfully by flotation.

**Tarnishing of Particles.**—The great differences in floatability between fresh and tarnished surfaces have already been stressed.<sup>1</sup> These differences arise from the fact that surfaces sufficiently tarnished to show a difference in color or iridescence possess oxidized coatings many molecules thick. Tarnished surfaces have flotative properties more like those of oxidized surfaces than like those of untarnished sulfide surfaces. Within a single ore, sulfide grains that differ widely in extent of tarnishing may occur, causing poor flotation results. This is because tarnished particles fail to float properly, remaining in the tailing and constituting a dead loss, or else appearing in a second concentrate (where selective flotation is used) as a detrimental diluent. The problem of dealing with tarnished sulfide particles is of importance and its solution will materially assist in reducing present losses.

Tarnishing of ore particles may have taken place in the ground before mining operations began; it may also have taken place during the mining operations themselves which allow mine water and air to act in turn upon the ore. Stock piles are a further source of oxidation<sup>(9)</sup>.

All sources of ore oxidation, with the exception of the natural tarnishing in place, can perhaps be remedied provided the cost of changing the mining, storing, and grinding operations is less than the advantage to be derived from the availability of an ore less extensively tarnished. Industrial research in that line is warranted as a source of operative economies.

### LIBERATION

The words *grain* and *particle* are used interchangeably by the layman to refer to a small piece of solid matter. *Grain* is also used by the microscopist to refer to a crystallographic unit as it is seen under the microscope on a polished or thin section of metal or rock. In this book *grain* is used in the sense in which it is used by microscopists, and *particle* is used to denote a small unattached piece of solid. Thus a particle may be composed of one or several grains. If all the particles in a ground ore are composed of one grain each they are said to be *free*, and the *liberation* of the minerals by grinding is perfect. If some particles are multi-granular, liberation is imperfect, the *percentage liberation* of any one mineral being the ratio of the mass of that mineral which is

<sup>1</sup> Chap. III, p. 35.

liberated to the total mass of that mineral. Particles containing grains of several species are *middling* particles, but particles containing several grains of the same species are generally considered free just as particles containing but one grain.

Liberation of the particles in an ore is accomplished by *comminution*, consisting of *crushing* and *grinding*. Crushing generally refers to the disintegration of relatively coarse particles, and grinding to that of fine particles.

From an ore-dressing standpoint, ideal comminution would consist in breaking the bonds between contiguous dissimilar grains without rupturing the grains. In most ores there is a marked tendency to fracture *between* grains in preference to *across* grains, although fracturing of free particles takes place to a greater or lesser extent<sup>(5)</sup>. Generally, the more solid the ore is, the greater the opportunity for fracturing across grains and the more difficult it is to take advantage of the tendency of the ore to break at grain boundaries. As the ground ore is reduced to a finer and finer state, liberation increases, as also the fracturing of grains already freed; this results in *overgrinding* of free particles.

Overgrinding goes with a useless expenditure of energy, a reduction in the capacity of the grinding equipment, and an increase in repair and upkeep costs for the grinding equipment. If such an overgrinding were to improve metallurgical performance there might be no objection and possibly an advantage to its use. Unfortunately overgrinding impairs results, due to the reduced floatability of the extremely fine particles. From an economic standpoint it is therefore desirable to come near complete liberation of the mineral grains in the ore, but to limit overgrinding to the strict minimum.

**Crushing and Grinding Practice.**<sup>1</sup>—Before proceeding to a determination of the liberation in a crushed ore it may be of interest to review briefly current crushing and grinding practice. Use of a single machine to accomplish all the reduction in size in one pass, although theoretically attractive, is impractical. Practice, indeed, has found that each type of comminuting device is suited over a narrow size-range, so that several crushing devices arranged in series must be used. Crushing and grinding in that fashion are known as *stage crushing* and *stage grinding*. Current

<sup>1</sup> For a detailed description of current practice consult: Taggart, "Handbook of Ore Dressing"; Richards and Locke, "Textbook of Ore Dressing"; Truscott, "Ore Dressing"; or other standard works.

practice is to use from four to eight stages to reduce the ore particles from mine run to a size suited for flotation operation.

It is customary to divide the field of crushing and grinding into coarse crushing, intermediate crushing, and grinding. The size limits for these three fields are rather indefinite, but 3 in. and  $\frac{1}{4}$  in. may be taken as averages for the points of division.

Jaw crushers and gyratory crushers are the typical *coarse-crushing* devices. In both, fracturing of the particles results from their being caught between a moving and a stationary jaw of hard metal. Jaw and gyratory crushers are suited for reduction from about 60 in. to about 1 in. At least two stages of crushing are required if the ratio of maximum particle size in the feed and product is as large as 36:2.

Cone crushers and rolls are the usual *intermediate-crushing* devices. Cone crushers are a new introduction and have won much favor for reduction from 6 in. to  $\frac{1}{2}$  in. Cone crushers operate on a crushing principle similar to that of gyratory crushers. Rolls are the standard machine for reducing from 2 in. to  $\frac{1}{8}$  in. Particles are crushed in them by becoming nipped between two revolving cylinders or rolls rotating toward each other. Two to four stages of intermediate crushing are generally used.

Rotating cylindrical or cylindroconical mills filled with a load of tumbling rods or balls dominate the *grinding* field. They are called *rod mills* or *ball mills* according to the grinding medium used. Rod mills cannot grind as fine as ball mills nor can they take as coarse a feed; for the production of a granular product, or if used in series with ball mills ahead of the latter they have received much favorable comment. Ball mills are standard equipment for fine grinding. The balls are made of cast iron, cast steel, or alloy steel, and range from 6 in. to 1 in. in diameter. Flint pebbles are sometimes used in place of steel balls; in that case the mills are known as tube mills.

Comminuting equipment is generally used in conjunction with sizing devices in order to limit more accurately the size of feed and product from each of the machines in use in the various stages. This results in material power economies and reduces overgrinding.

Sizing devices are of two kinds, screens and classifiers. *Screens* separate particles according to their actual size; they are neither efficient nor economical for separating particles at a size finer than





centrator; and Fig. 27, the fine-crushing and grinding flow-sheet of the Sullivan, B. C., lead-zinc concentrator.

At Anaconda the ore is fed from a receiving bin ① to a bar screen or grizzly ②, having a  $3\frac{1}{2}$ -in. spacing; the oversize is crushed in a gyratory crusher, having a 20-in. gape ③, whose discharge joins the undersize from ② and passes on one 4-ft., type 39, single-surface, tandem, "Hummer" vibrating screen ④, having 1.5-in. square openings. The oversize from the Hummer screen is crushed in a 7-ft. Symons cone crusher ⑤ set at  $\frac{3}{4}$  to 1 in. The undersize from ④ and the crushed product from ⑤ go to the fine storage bin ⑥. The two screens ②, ④, and two crushers ③, ⑤, are in duplicate to avoid breakdown delays. The fine-ore bin feeds seven sections.

The feed to each section first goes to four 36-in. by 6-ft. trommels (screens), having  $\frac{7}{8}$ -in. round holes ⑦; the oversize from ⑦ is crushed in one set of 55- by 24-in. rolls ⑧, in closed circuit; the undersize from ⑦ passes on four 36-in. by 6-ft. trommels, having  $\frac{3}{8}$ -in. round holes ⑨; the oversize from ⑨ is crushed in two sets of 55- by 24-in. rolls ⑩ in closed circuit with ⑦; the undersize from ⑨ is sized by eight 36-in. by 6-ft. trommels ⑪, having  $1\frac{1}{2}$ - by 12-mm. slotted openings, whose undersize goes directly to a five-way pulp distributor ⑭. The oversize from ⑪ goes to six additional 36-in. by 6-ft. trommels ⑫, having  $1\frac{1}{2}$ - by 12-mm. slotted openings, operating in closed circuit with two sets of 55- by 24-in. rolls ⑬; the undersize from ⑫ goes to pulp distributor ⑭. Pulp distributor ⑭ feeds five 9-ft. Anaconda hydraulic classifiers ⑮, whose overflow contains the finest portion of the pulp and is treated further in the slime plant (Fig. 45*b*, page 183). The underflow from ⑮ is deslimed further in five Allen sand cones ⑯ whose underflow feeds five 8-ft., 4- by 62-in. Hardinge ball mills ⑰ in closed circuit with five 4-ft. Dorr classifiers ⑱. The overflow from the Allen cones feeds also into the Dorr classifiers, whose overflow is the feed to the flotation sections (Fig. 45*a*, page 183).

At the Sullivan mill (Fig. 27) the ore is fed from an 1800-ton receiving bin ① to a coarse screen ②, whose oversize goes to a Symons cone crusher ③. The undersize from ② and discharge from ③ are crushed further by two 72- by 20-in. Allis Chalmers rolls ④, in open circuit. The discharge from the rolls is stored in bin ⑤, which feeds five 10-ft. by 48-in. primary Hardinge ball mills ⑥, in parallel. These mills are in open circuit with as

many primary Dorr quadruplex classifiers ⑦. The sand from ⑦ is ground further in four 8-ft. by 48-in. and four 10-ft. by 48-in. secondary Hardinge mills ⑧ in closed circuit, through pulp distributors ⑨, with 10 secondary Dorr standard duplex and eleven 72-in. Akins classifiers ⑩. The overflow from the primary and secondary classifiers is apportioned to four tertiary classifiers ⑫ (two standard-duplex and two bowl classifiers) by a pulp distributor ⑪. The tertiary classifiers are in closed circuit with two

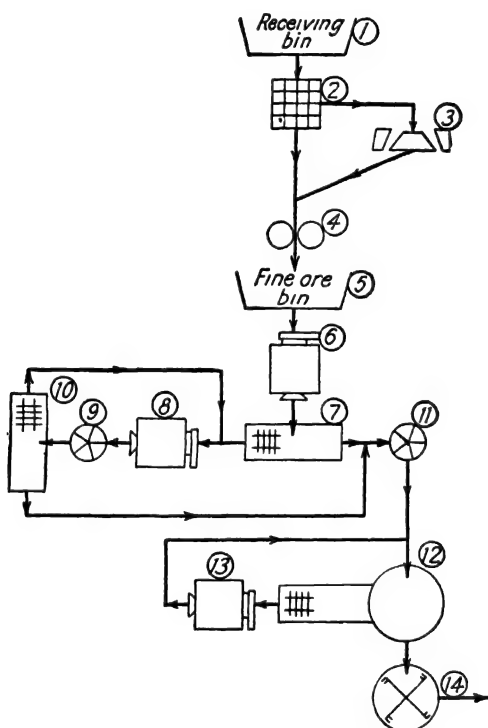


FIG. 27.—Sullivan crushing and grinding flow-sheet (1930).

tertiary 8-ft. by 48-in. Hardinge mills ⑬; their overflow goes to a surge tank ⑭, thence to the flotation division (Fig. 64, page 236).

Although there are variations between the various crushing and grinding flow-sheets that would justify considerable study from a crushing and grinding standpoint, the similarity between them is sufficient from a flotation standpoint, to consider the Anaconda and Sullivan flow-sheets as typical.

**Recent Grinding and Classifying Trends.**—Recent developments in the crushing and grinding circuits of flotation plants have featured the introduction of cone crushers for intermediate crushing and the adoption of more elaborate fine-grinding flow-sheets. The use of cone crushers is largely the result of the striking economy of this machine. The developments in the fine-grinding field have resulted from the excellent performance of selective flotation which imposed more perfect liberation of the minerals, particularly of the sulfides from each other, as the principal means of furthering improvements in metallurgical results. Recent developments in fine grinding have also been prompted by the desire to effect selective grinding and to minimize overgrinding.

The fact that substantially complete liberation of the non-sulfide grains is often obtained from grinding at a much coarser size than is necessary for liberation of sulfides from each other has resulted in the growing adoption of schemes involving regrinding collective concentrates before refloating them selectively. This is exemplified by the practices at the Miami concentrator (Chap.

VIII, page 185), and the Britannia concentrator (Chap. VIII, page 187). So far this principle has not been applied extensively outside sulfide-copper flotation plants. A somewhat different practice has been developed for the treatment of lead-zinc ores in which liberation of the lead from the zinc requires finer grinding than the liberation of these sulfides from the gangue. It consists in cutting from the lead froth a rougher concentrate, formed under conditions of delicately adjusted flotation, separately from a middling concentrate formed under more

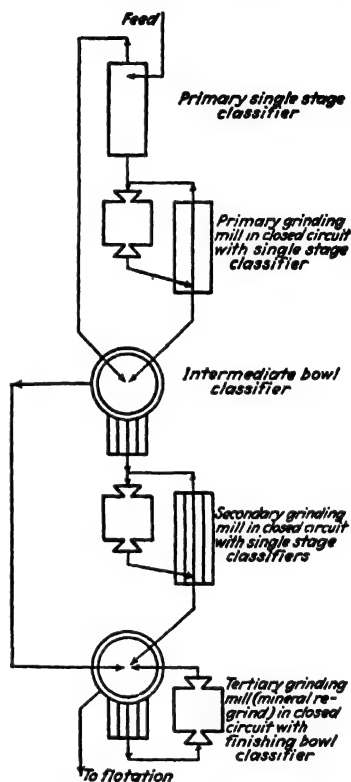


FIG. 28.—Ideal grinding flow-sheet.  
(After Dorr and Marriott.)

powerful flotation conditions; this middling concentrate contains a large number of middling particles needing further grinding, and is ground further, before being subjected to a second selective flotation operation. Regrinding of the middling concentrate may take place in a different circuit from the main grinding circuit, as at the Morning mill (Chap. IX, page 227), or in the main grinding circuit, as at the Sullivan mill (Chap. IX, page 236).

When rugged, simply constructed ball mills were introduced, their superiority became so apparent that it was attempted to

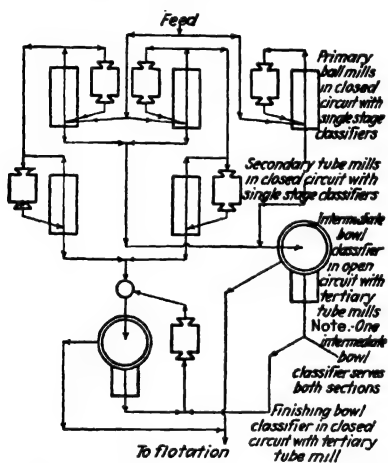


FIG. 29.—Recent (1930) fine-grinding practice at Allenby plant, Granby Consolidated Copper Co., B. C. (After Dorr and Marriott.)

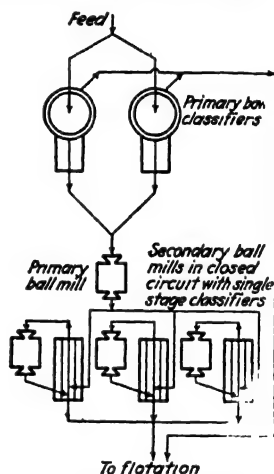


FIG. 30.—Recent (1930) fine-grinding practice at Arthur plant, Utah Copper Co. (After Dorr and Marriott.)

make them cover a greater and greater range of size reduction. With the advent of selective flotation and the requirement of finely ground pulps it has been found that in large plants it is more effective to limit the size range through which particles fed to ball mills are ground. This is achieved by (a) using several ball mills in series, each being fitted with balls suited to the size of particles it is to crush; (b) limiting the size of particles fed to and discharged from each ball mill by means of classifiers in closed circuit with the mills. Figure 28 shows what Dorr and Marriott<sup>(4)</sup> consider as an ideal grinding flow-sheet. This is approximated in practice, as may be seen from Figs. 29 and 30 which represent modern fine-grinding practices from two large copper plants.

**Grinding-classifying Circulating Loads.**—The practice of carrying a high grinding-classifying circulating load has been recommended<sup>(2)</sup> on the ground of economy. Modern tendency to increase classifier capacity in relation to the crushing units associated with it results in increased circulating loads and in more effective grinding.

Increased classifier capacity in relation to fine-grinder capacity results in more frequent removal, from the mill, of particles that are already ground sufficiently fine. As a result, the proportion of particles on which overgrinding can proceed is minimized. Theoretically the coarser particles only are crushed in a grinding mill such as a tube, ball, or rod mill because of the protecting sizing action of the mill<sup>(5)</sup>. This action, however, is not so perfect as the positive protection against further grinding offered by a classifier. High circulating loads are one of the most effective ways to lessen overgrinding.

**Classifiers.**—Practically all *classifiers* in use at present are of the *rake* or *worm* types, typified by the Dorr and Akins classifiers. These classifiers are cheap to operate, and need little attention, power, and water. However, their efficiency is not as high as might be wished, and the sand returned to the mills generally contains a considerable percentage of material that should overflow the weir of the classifiers. Bowl classifiers, which are especially designed for a finer separation than the ordinary rake classifiers, are said to be more effective, but even bowl classifiers fall short of perfection. Better classification is obtained in *hydraulic classifiers*, but hydraulic classifiers require so much more water than bowl, rake, or worm classifiers, that their use necessitates thickening before floating.

To be operated most effectively, classifiers, particularly when making a split at a fine size, necessitate more water than it is desirable to have in a flotation pulp. This is receiving increased attention, and it is likely that the practice of thickening before flotation will expand in the future. This may even induce the use of classifiers of the hydraulic type.

**Degree of Liberation.**—Microscope inspection of sized portions of a ground ore shows that liberation is more nearly perfect in the finer sizes. As a result, examination of the coarsest portion of an ore pulp affords a critically adverse picture of liberation. This is shown strikingly in Sec. IV of Table 16, the liberation of galena going from 43 to 65, 83, 94, and 99 per cent for each

reduction in average size of  $\sqrt{2}$ . Similarly, the liberation of the sphalerite goes from 53 to 71, 87, 96, and 99 per cent.

TABLE 16.—MICROSCOPE DETERMINATION OF LIBERATION OF MINERALS IN A COMPLEX LEAD-ZINC ORE WHICH WAS ELUTRIATED AFTER GRINDING. ORE CONTAINED 8.4 PER CENT LEAD AND 7.7 PER CENT ZINC

Size range	A	B	C	D	E	F
I. Size microns						
Galena	105/75	75/52	52/37	37/26	26/18	- 18
Sphalerite	150/105	105/75	75/52	52/37	37/26	- 26
Gangue	210/150	150/105	105/75	75/52	52/37	- 37
II. Percentage by weight (from quantitative microscope determination)	100 0	100 0	100.0	100.0	100.0	100.0
Free galena	7.1	8 0	8.6	8 4	8.1	9.3*
Free sphalerite	10.3	11 6	11.3	10.7	10.3	10.4*
Free gangue (all other free particles)	59.2	68.0	75.6	79.9	81.5	80 3
Mixed galena-sphalerite (average one-half each)	16.3	8 3	3.2	0.9	0.1	
Mixed galena-gangue (average one-fourth galena)	3.7	1 9	0 7	0.1	0 0	
Mixed sphalerite-gangue (average one-fourth sphalerite)	2 4	1 2	0 5	0.0	0.0	
Mixed galena-sphalerite-gangue (average one-fifth each sulfide)	1 0	0 4	0.1	0.0	0.0	
III Percentage of each size in relation to total weight	1.5	7 3	14 6	16.2	9.7	50 7
IV. Percentage liberation at each size						
Galena	43	65	83	94	99	100*
Sphalerite	53	71	87	96	99	100*
Gangue	92	97	99	100	100	100*
V. Average liberation for whole pulp: galena 91.3 per cent, sphalerite 92.8 per cent, gangue 99 per cent.						

\* Calculated.

Although inspection of only the coarsest part of an ore pulp is critically severe in respect to the liberation that has been accomplished, it supplies a crude picture of grinding requirements. It is more desirable, however, to quantify the degree of liberation for any one set of grinding conditions by means of quantitative determinations of the percentage liberation.

The following experimental steps are involved in quantifying the degree of liberation (Table 16): (a) sampling the ground pulp, (b) elutriating the sample, (c) weighing each elutriated fraction, (d) making briquettes from each elutriated fraction, and (e) determining microscopically the number of free and

mixed particles belonging to each mineralogical species. From the number of particles of each kind it is possible to calculate the percentage by weight of each kind. This involves a weighting factor depending on the density of each mineral species and on the volume occupied by particles of each type. The average volume of particles of each type may in turn be determined from the relationship between density and size deriving from Stokes' law for the settling of particles in a viscous fluid. The percentage liberation of each mineral species at each size, and for the whole pulp, is readily obtained from the weighted distribution of particles of each type in each size group.

In comment of the data presented in Table 16 it might be observed that the liberation of the two sulfides from each other is much less complete than the liberation of the gangue from either sulfide. This indicates the possibility of using a flow-sheet adapted to reject the gangue before complete liberation of the sulfides is achieved, and of regrinding a mixed lead-zinc concentrate or cleaner tailing in a secondary grinding circuit. Application of this principle is not lacking.

**Economic Limit to Liberation.**—It is not practical to carry liberation to completion; indeed, it is economically desirable to strike some happy medium between complete liberation and one that is metallurgically ineffective. The economic liberation depends upon the metal content of the ore, plant tonnage, and especially upon the fineness of aggregation of the ore. The higher the metal content in the ore, the larger the plant tonnage; and the coarser the mineral aggregation in the ore, the more desirable it is to approximate complete liberation. Although data on the subject are scarce, it is probable that in most mills an average over-all liberation of 90 per cent or better is obtained.

**Flotation of Middling Particles.**—The flotation of particles composed of more than one mineral is of interest and deserves considerable study particularly since particles of that type are frequently encountered. If middling particles are composed of more than one mineralogical species at their surface, their flotative behavior is intermediate between that of the two species. Depending upon the percentage of surface occupied by each mineral, middling particles are more like the one or the other of their components. The presence of a large percentage of middling particles in an ore pulp dampens the selectivity between

minerals and makes the separations less distinct. This is a drawback, but it can be overcome by separating as a middling product those particles that require further grinding. Such a middling product can be obtained by cleaning a rougher concentrate or by further floating (scavenging) a rougher tailing under very active flotative conditions. It is likely that in the future more attention will be paid to the treatment of middling particles, as the ores to be treated are becoming increasingly complex, and that middling particles will be relatively more abundant.

#### PARTICLE SIZE AND FLOATABILITY

In Chaps. III, IV, and V, flotation was presented under its chemical aspects; in particular it was pointed out that flotation is the result of non-polarity of mineral surfaces and that non-flotation is the result of polarity of mineral surfaces. It may be well to inquire whether non-polar particles of all sizes float equally well and, similarly, whether polar particles of all sizes sink equally well. *A priori* floatability may be expected to increase with fineness of particle, alike for particles having polar surfaces and for particles having non-polar surfaces. Conversely very coarse non-polar particles may well show such reduced floatability as to become substantially unfloatable. Experiment indicates that this picture is not correct in what

TABLE 17.—TYPICAL AVERAGE PARTICLE SIZE IN PULPS OF SULFIDE ORES

Size range		Weight, per cent
Microns	Mesh	
+295	+48	0.5
295/208	48/65	3
208/147	65/100	7
147/104	100/150	13
104/74	150/200	17.5
74/52	200/280	14
52/37	280/400	10
37/26	400/560	7
26/13	560/1120	9
13/6.5	1120/2240	6
6.5/0.5	2240/30,000	11*
-0.5 (colloidal)	-30,000	2*

\* The relative amounts of colloidal and non-colloidal material are estimated by extrapolation, but the total  $-6.5\mu$  material is known fairly accurately.



regards the behavior of very fine particles, but that it is correct concerning very coarse particles.

**Size of Particles in Flotation Pulp.**—In accordance with differences in their structural character, different ores yield

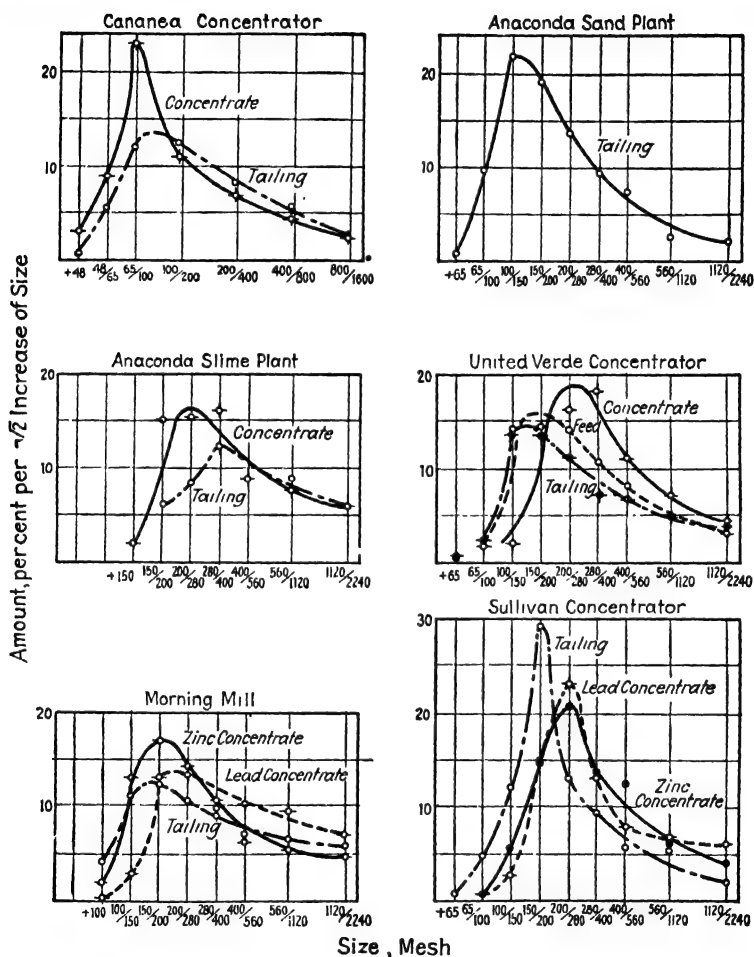


FIG. 31.—Size distribution of flotation pulps.  
Anaconda, United Verde, Morning, Sullivan and Cananea mills, 1929.

pulps of different fineness, that is pulps in which the distribution of particles in the various sizes is individualistic to a substantial extent (see Tables 18 to 21, and Fig. 31). In spite of this, there are many generic traits of flotation pulps concerning the relative

distribution of particles of various sizes. These generic features are brought out by Table 17 in which is given an average size distribution obtained from data on the pulps from eight different plants.

The size of particles is generally stated in terms of meshes, that is in terms of the number of wires per linear inch in woven-wire sieves. This usage has grown out of the extensive use of testing sieves in connection with gravity concentration, crushing, and grinding, but it is largely meaningless in connection with flotation, except as a convention. This is because no sieve finer than the 400-mesh sieve has been built. Statement of size of all particles in terms of microns would be more scientific but this

TABLE 18.—EFFECT OF PARTICLE SIZE ON FLOTATION; MORNING MILL, FEDERAL MINING AND SMELTING COMPANY

	Size, mesh								
	+100	100/ 150	150/ 200	200/ 280	280/ 400	400/ 560	560/ 1120	1120/ 2240	—2240
Chemical analysis of lead concentrate									
Lead, per cent	78.8	80.2	78.1	74.6	73.8	70.6	70.4	74.0	71.7
Zinc, per cent	3.2	3.3	3.3	5.0	6.0	6.8	6.8	6.6	9.6
Iron, per cent	2.6	1.5	1.6	2.5	3.0	2.6	1.8	1.2	1.4
Insoluble, per cent	1.2	0.6	0.6	1.0	1.0	1.0	1.2	1.6	2.7
Chemical analysis of zinc concentrate									
Lead, per cent	5.0	2.3	2.0	1.8	1.4	1.4	1.4	3.2	5.0
Zinc, per cent	50.8	51.2	51.2	50.3	50.3	51.6	55.6	55.7	57.4
Iron, per cent	7.1	7.8	8.0	8.2	8.4	7.5	4.6	3.9	2.9
Insoluble, per cent	1.4	1.4	1.9	2.4	2.4	2.2	1.3	2.6	5.5
Chemical analysis of tailing									
Lead, per cent	1.4	0.75	0.65	0.60	0.50	0.35	0.50	0.40	1.02
Zinc, per cent	1.8	0.95	0.40	0.35	0.20	0.15	0.15	0.15	1.50
Iron, per cent	12.5	14.8	16.6	18.0	18.4	18.7	19.0	16.1	13.0
Insoluble, per cent	59.2	55.2	53.0	49.2	48.4	45.8	45.0	55.0	53.8
Lead recovery in lead concentrate, per cent	49.3	74.5	92.7	94.4	94.7	97.0	96.2	95.2	86.2
Zinc recovery in zinc concentrate, per cent	62.7	87.9	95.2	95.7	97.2	97.2	97.2	97.3	78.8
Selectivity indices									
Lead circuit									
Lead to zinc	7.7	13.4	14.2	11.7	11.0	10.8	9.3	9.3	5.4
Lead to siderite	14.7	28.2	30.2	25.4	26.0	32.6	35.0	37.8	21.7
Lead to quartz	46.6	83.4	85.0	65.1	70.4	80.8	65.0	60.2	31.8
Zinc circuit									
Zinc to lead	3.1	4.1	6.4	7.2	10.0	9.5	11.7	6.8	2.3
Zinc to siderite	7.7	10.1	16.2	18.5	24.2	20.8	39.6	39.5	13.6
Zinc to quartz	37.8	46.1	59.5	56.5	72.1	85.2	114.0	89.3	20.3

TABLE 19.—EFFECT OF PARTICLE SIZE ON FLOTATION; SULLIVAN CONCENTRATOR, CONSOLIDATED MINING AND SMELTING COMPANY OF CANADA, LTD.

	Size, mesh								
	+100	100/ 150	150/ 200	200/ 280	280/ 400	400/ 560	560/ 1120	1120/ 2240	- 2240
Chemical composition of lead concentrate									
Lead, per cent.	71.8	72.4	74.0	69.8	69.8	69.4	70.6	71.6	65.8
Zinc, per cent.	0.9	2.3	3.2	5.4	6.9	7.0	5.6	3.8	3.7
Iron, per cent.	3.9	4.5	5.2	6.0	4.7	4.2	3.5	3.0	4.0
Chemical composition of zinc concentrate									
Lead, per cent.	4.3	4.1	3.6	2.9	2.2	1.8	2.4	4.5	9.2
Zinc, per cent.	47.6	46.8	43.7	48.4	52.3	52.9	51.9	49.6	40.3
Iron, per cent.	13.6	14.1	17.7	13.8	10.6	9.8	9.7	8.5	8.2
Lead recovery in lead concentrate, per cent.	34.3	62.5	83.8	92.4	93.5	93.5	92.4	90.3	74.2
Zinc recovery in zinc concentrate, per cent.	23.2	83.6	81.6	95.8	96.9	97.9	96.3	95.9	82.8

use has not gained much favor in practical circles. In Table 17 the size of the particles is stated in terms both of meshes and of microns.

TABLE 20.—EFFECT OF PARTICLE SIZE ON FLOTATION; SLIME PLANT, ANACONDA COPPER COMPANY CONCENTRATOR

	Size, mesh						
	+200	200/ 280	280/ 400	400/ 560	560/ 1120	1120/ 2240	— 2240
Chemical analysis of concentrate							
Copper, per cent.	18.94	20.56	27.70	20.02	22.30	22.80	13.24
Iron oxide (FeO), per cent.	38.1	36.2	30.1	35.9	29.6	20.9	9.4
Silica, per cent.	3.0	3.2	7.3	7.3	8.5	17.0	32.8
Chemical analysis of tailing							
Copper, oxidized, per cent.	0.067	0.059	0.072	0.084	0.116	0.173	0.434
Copper, sulfide, per cent.	0.410	0.111	0.091	0.077	0.067	0.099	0.183
Iron oxide (FeO), per cent.	3.3	1.9	2.1	2.1	2.3	2.6	2.7
Silica, per cent.	78.9	74.7	79.2	81.3	69.7	62.0	47.8
Alumina, per cent.	6.5	8.2	10.7	11.9	16.9	19.7	25.0
Recoveries in concentrate							
Total copper, per cent.	96.2	98.1	98.1	96.7	96.3	95.0	70.8
Sulfide copper, per cent.	96.8	98.7	98.9	98.2	98.6	98.1	91.1
Pyrite, per cent.	90.0	92.4	86.0	85.1	78.1	69.8	33.2
Non-sulfide gangue, per cent.	5.7	5.0	2.7	2.4	3.8	6.9	6.6

From Table 17 it appears that for size intervals in constant ratio, proceeding from coarse to fine particles, the bulk of pulps increases rapidly to a maximum, then decreases at a lessened rate to a vanishing point which is beyond the range of experimental perception. The bulk of  $-2240$  mesh ( $6.5\mu$ ) material is surprisingly large (13 per cent), but the bulk of truly colloidal material ( $-0.5\mu$ ) is probably small.

**Results from Practice.**—Tables 18, 19, 20, and 21<sup>(6)</sup> illustrate the effect of particle size on metallurgical results at several plants. Tables 18 and 19 present the results obtained at two lead-zinc plants, the Morning and Sullivan concentrators (see Chap. IX for descriptions and flow-sheets of flotation division). Tables 20 and 21 present the relationship of particle size to metallurgical results at the slime plant of the Anaconda Copper Company (see Chap. VIII for description and flow-sheet), and the Clarkdale plant of the United Verde Copper Company. Although there are substantial differences between the performances at these

TABLE 21.—EFFECT OF PARTICLE SIZE ON FLOTATION; UNITED VERDE COPPER COMPANY CONCENTRATOR

	Size, mesh								-2240
	+100	100/ 150	150/ 200	200/ 280	280/ 400	400/ 560	560/ 1120	1120/ 2240	
Chemical analysis of feed									
Copper, per cent ..	2 07	*	3.93	3.35	3.91	4 95	3.81	3 60	1.32
Iron, per cent ..	10 4	*	16 4	19 6	20.3	24 8	19 8	18.9	10 0
Chemical analysis of concentrate									
Copper, per cent ..	20.10	17.65	17.25	15.47	14.82	15 73	16 85	18 10	13 05
Iron, per cent .....	28.8	27.7	30 0	31.7	33 2	32 4	31 5	28 5	21.5
Chemical analysis of tailing									
Copper, per cent	0.372	0 385	0 253	0.223	0.142	0.142	0 116	0 132	0 182
Iron, per cent . . .	9.4	9 5	14.6	15.7	14.9	19.1	19 9	17 4	9 6
Copper recovery, per cent . . . . .	77 2		95.4	96.8	98.7	98.2	98 5	97 6	92 0
Pyrite rejection, per cent .....	84 0		61.7	54.7	36.3	55.9	61.7	70.4	†
Selectivity index, copper pyrite.....	4 2		5 8	6.1	6.6	8.3	10 3	9 8	†

\* Sample was lost.

† Not calculated because of uncertain amount of iron-bearing silicate gangue.

plants, the similarities are striking. In particular, it should be noted that optimum recovery of the metal to be recovered and optimum rejection of the minerals to be rejected result in optimum selectivity in the intermediate size range of 10 to 50 microns. The occurrence of optimum selectivity in the same size range in all instances strongly suggests that this circumscription of best flotation performance is not so much the result of chemical effects, but rather of some structural or physical effect that is the same in all cases.

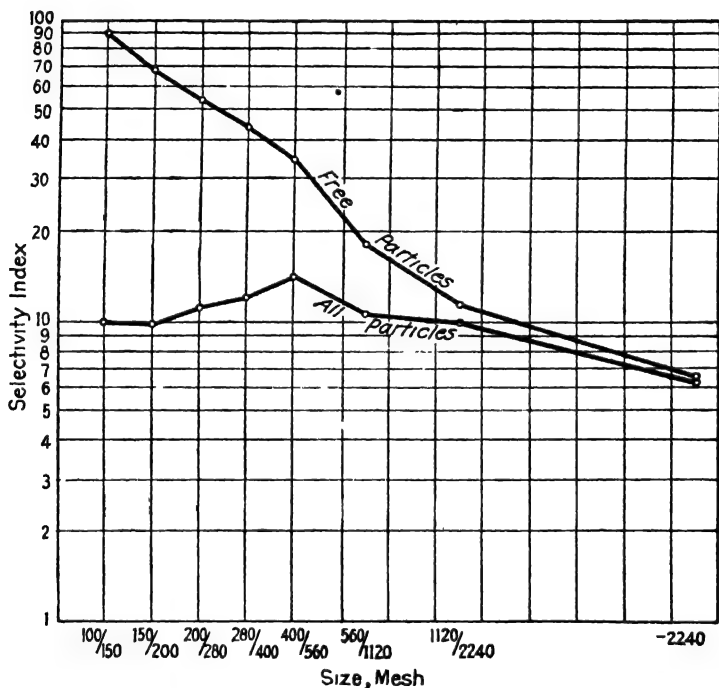


FIG. 32.—Selection of minerals at Sullivan plant.

Above: If effect of free particles only is considered; below: if effect of all particles is considered. Lead cycle.

**Behavior of Polar Particles.**—The greater recovery of the polar minerals in the finest sizes is explained by the lesser settling velocity of fine particles which causes their overflowing “mechanically” between bubble walls. The slightly greater recovery of the polar minerals in the coarsest sizes as compared with medium-coarse sizes may be due to the presence of these minerals

in middling particles, or to their becoming entrapped in the bubble filter of the froth.

**Behavior of Non-polar Particles.**—The lower recovery of the non-polar minerals in the coarsest sizes is due to the presence of non-floating middling particles in the coarse sizes, as well as to the lessened floatability of very coarse particles resulting from the difficulty in supporting them at bubble walls<sup>(6)</sup>. It has already been pointed out that middling particles are more plentiful in the coarsest sizes of a ground pulp and that it is uneconomical to practice complete liberation of the minerals in an ore. In all the plants covered by Tables 18 to 21 middling particles are found in the coarsest sizes. Some of these middling particles are lost in the tailing, thus decreasing the mineral recovery in the coarse sizes. Also, since other middling particles are recovered, the gangue recovery in the concentrate is increased and the selection appears poorer in the coarsest sizes than at some intermediate size. That this is the proper interpretation for the apparent maximum selectivity in the range of 10 to 50 microns is shown by Fig. 32 for the performance of the Sullivan plant.

**Behavior of Very Fine Non-polar Particles.**—The lesser recovery of the metals in the finest sizes, which obtains at all plants, is unexpected and indeed contrary to the early views on flotation. As decreased floatability because of decreased size appeared at first an unlikely situation it was surmised that this decreased floatability might be caused by the presence of a greater proportion of oxidized particles in the finest portion of ore pulps.<sup>1</sup> This is supported by the fact that a greater percentage of the metal is in an oxidized condition in the finer sizes than in the coarser sizes.<sup>2</sup> However, the decrease in recovery of lead, copper, and zinc occurring in the form of sulfides is out of all proportion to the effect that would be expected from partial surface oxidation of the fine particles.

<sup>1</sup> B. S. Morrow, Anaconda, is of the opinion that non-recovery of extremely fine non-polar particles is due to imperfect pulp dispersion. Although this may be a contributing cause, it does not seem to account fully for the facts. Indeed it does not explain the observed size sequence of floatability (p. 151), nor the fact that colloidal particles are irrecoverable in a dispersed pulp consisting of water and one mineral only.

<sup>2</sup> As determined by analyses for metals in oxide or carbonate form. These analyses, however, may be grossly misleading as very fine sulfide particles have much surface, on which oxidation proceeds continuously.

To test the importance of oxidation in the fine sizes as a factor affecting the flotation of sulfide minerals a synthetic mixture

TABLE 22.—METALLURGICAL RESULTS OBTAINED ON SYNTHETIC GALENA-GANGUE MIXTURE

Product	Size			Weight, grams	Assay, per cent		Recovery, per cent	
	Mesh	Microns (quartz and feldspar)	Microns (galena)		Lead	Gangue*	Lead	Gangue*
Cleaner concentrate	+100	+147	+74	5.1	83.8	3.2	99.0	1.6
	100/200	74/47	37/4	15.9	77.1	11.0	99.5	1.6
	200/400	37/4	18/7	14.9	58.4	32.7	98.6	2.5
	400/800	18/7	9/8	17.0	49.8	42.5	97.4	5.8
	-800	-18	-9	16.2	37.8	56.4	79.8	8.0
Middling (cleaner tailing)	+100	+147	+74	10.1	0.10	99.9	0.02	14.2
	100/200	74/47	37/4				0.07	8.8
	200/400	37/4	18/7	23.9	0.08	99.9	0.23	12.5
	400/800	18/7	9/8	35.0	0.07	99.9	0.29	28.4
	-800	-18	-9	29.7	1.65	98.1	6.33	25.8
Rougher tailing	+100	+147	+74	5.3	0.05	99.9	0.07	84.2
	100/200	74/47	37/4	97.5	0.06	99.9	0.47	89.6
	200/400	37/4	18/7	162.2	0.07	99.9	1.17	85.0
	400/800	18/7	9/8	81.4	0.25	99.7	2.30	66.8
	-800	-18	-9	76.4	1.50	98.2	14.87	66.2

\* Calculated.

TABLE 23.—SELECTIVITY INDICES, LEAD TO GANGUE, FOR TEST RESULTS PRESENTED IN TABLE 22

	Size, mesh				
	+100	100/200	200/400	400/800	-800
Microns					
Quartz and feldspar.....	+147	74/47	37/4	18/7	-18
Galena.....	+74	37/4	18/7	9/8	-9
Selectivity indices					
Considering roughing operation only.....	72.9	49.4	21.8	9.05	3.24
Considering cleaning operation only.....	211	88.4	45.8	40.0	6.3
Considering the two operations (equivalent to discarding cleaner tailing).....	262	106	54	24.7	6.6
Geometric average of the selectivity indices.....	160	78	40	22	5

of coarse unoxidized galena and granite was ground and floated. The results (Tables 22 and 23) show that in this case, as well as in the case of ores, very fine particles of non-polar character are not recovered so completely as coarser particles. In the case of pure galena and granite the explanation that fine particles are more extensively oxidized cannot be invoked because the particles of galena fed to the grinding mill were as free of oxidation as possible and that, had oxidation proceeded during grinding, it should have spread more or less evenly over particles of all sizes.

To further prove that fineness of the particles, *and no other cause*, is responsible for lack of recovery of fine particles several charges of pure galena and pure granite were ground in a porcelain-jar mill so as to reduce all the particles to a size finer than 3 or 4 microns. The paint-like pulps were floated with varying amounts of amyl xanthate. The results are presented in Table 24. It is seen that even with as much as 4 lb. amyl xanthate per ton the lead recovery is poor.

TABLE 24.—FLOTATION RESULTS WITH PAINT-LIKE PULPS OF GALENA AND GRANITE ( $-4\mu$ )

Test number	Reagents used, lb. per ton		Product	Lead content, per cent	Lead recovery, per cent	Lead-gangue selectivity index for roughing operation
	Terpineol	Amyl xanthate				
1	0.05	1.0	Cleaner concentrate	35.8	34.0	1.54
			Cleaner tailing	14.0	20.8	
			Rougher tailing	12.5	45.2	
2	0.05	4.0	Cleaner concentrate	34.5	67.7	1.93
			Cleaner tailing	8.1	9.7	
			Rougher tailing	7.9	22.5	

Experiments show that the same sort of results obtain with other sulfides as obtain with galena. It may then be concluded that the non-recovery of metal in the fine sizes of flotation pulps is due not only to the greater abundance of oxidized minerals in those sizes but also to non-flotation of particles that apparently are perfectly suited to float except for their fineness.



**Non-recovery of Fine Non-polar Particles and Brownian Movement.**—It is of interest to note that decreased recovery of the floatable mineral occurs in particles as coarse as 5 microns (3000 mesh), that is, at a size much coarser than is required to display visible Brownian movement (*ca.* 0.5 micron).

**Sequence of Flotation of Particles of Various Sizes.**—As a factor contributing further to an understanding of the reason for the lessened recovery of very fine particles it should be noted that the coarsest particles are recovered first and the finest last. This

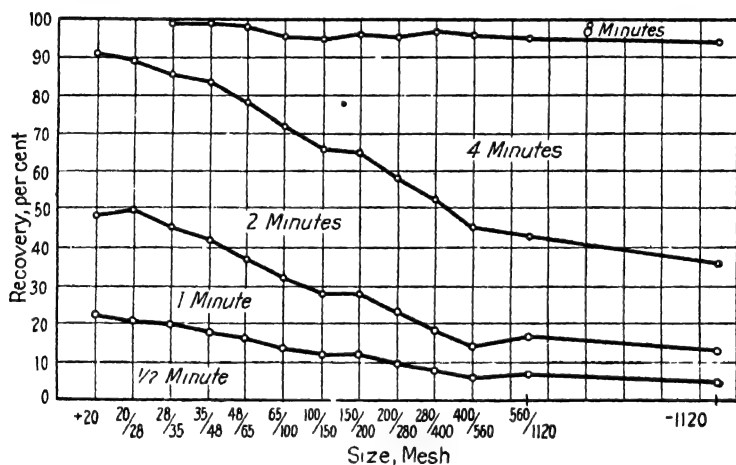


FIG. 33.—Time sequence of flotation of galena particles of various sizes.

is strikingly shown by experiments run on mixtures of pure galena and pure granite (Fig. 33). In comment of the data presented in Fig. 33 it might be mentioned that the decreasing time rate at which coarse particles are recovered is not due to increasing paucity of frother concentration as the experiment proceeded, since repetition of the experiment in the presence of a great excess of frother has led to results similar to those presented in Fig. 33. The only interpretation that can be placed on the results is that there is a *gradual* decrease in readiness to adhere to air bubbles from coarse to fine particles, and that this tendency is manifested by an acutely perceptible reduction in recovery on proceeding from medium-fine (300 to 1000 mesh) particles to very fine particles (under 6000 mesh). These facts are in line with the direct-encounter hypothesis of gas-solid attachment (Chap. VI).

It has been mentioned above that in most plants the recovery of very coarse (over 100 mesh) non-polar particles is smaller than that of medium-coarse particles (Tables 18 to 21). This is noticeable, although to a lesser extent, when mixtures of pure galena and pure granite (Table 22) are floated under conditions of intense floatability for galena (pH 7.0 to 7.5, amyl xanthate in abundance). The decrease in recovery with increasing coarseness generally appears at a coarser size with pure minerals than in practice.

**Theoretical Upper Size Limit of Floatable Particles.**—The difference in the size at which decreased floatability due to excessive coarseness is noticeable in the case of the pure minerals and

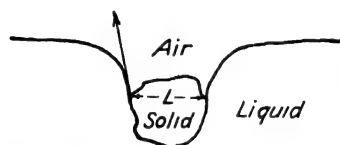


FIG. 34.—Mineral particle at a liquid surface.

Coarse particle is supported by the surface tension of the liquid.

in the case of ores makes of interest a search for a theoretical upper size limit of floatability. Let Fig. 34 represent a particle of mineral of density  $D$  and volume  $V$  supported at the surface of a liquid of density  $d$ , and let the length of the three-phase boundary be  $L$ . The weight supported by each unit of boundary

length is  $V(D - d) \times 1/L$ . This weight is supported by the surface tension of the liquid. Clearly, the surface tension will exert maximum support when it is directed vertically at the point of support, so that the maximum particle size for particles of a given shape can be obtained from a consideration of the size-mass relationship by geometry, and by Eq. (1):

$$T_{GL} = \frac{V(D - d)}{L}. \quad (1)$$

Table 25 gives the calculated maximum sizes for galena cubes, pyrite cubes, sphalerite tetrahedra, calcite rhombohedra, and coal spheres that can be supported by the surface tension of an aqueous solution having a surface tension of 70 dynes per centimeter.

The sizes given by Table 25 are much in excess of the sizes currently floated in practice. However, the actual sequence of maximum coarseness at which flotation is possible is the same, namely: coal, calcite and sphalerite, pyrite, and galena.

The calculations for Table 25 were made on the hypothesis of the existence of quiescent circumstances. It is of interest to note that it is experimentally possible to cause large non-polar-

TABLE 25.—CALCULATED SIZE OF PARTICLE OF DENSITY  $D$  THAT CAN BE SUPPORTED BY THE SURFACE TENSION (70 DYNES PER CENTIMETER) OF AN AQUEOUS PULP OF DENSITY  $d$

Mineral	Density of mineral, $D$	Density of pulp, $d$	Size of particles, * $a$ , mm.
Galena.....	7.5	1.5	2.2
Pyrite.....	5.0	1.5	3.5
Sphalerite.....	4.1	1.5	5.6
Calcite.....	2.7	1.25	4.6
Coal.....	1.35	1.10	13.1

\* For pyrite and galena,  $a$  is the edge of a cube.

For sphalerite,  $a$  is the edge of a regular tetrahedron.

For calcite,  $a$  is the edge of a regular rhombohedron.

For coal,  $a$  is the diameter of a sphere.

surfaced particles of mineral to float, and that the dividing point between floating and non-floating particles agrees with the calculations of Table 25. Figure 35 presents the results obtained.

In agitated pulps, conditions are different from those at the surface of quiescent water. Assuming that particles are carried

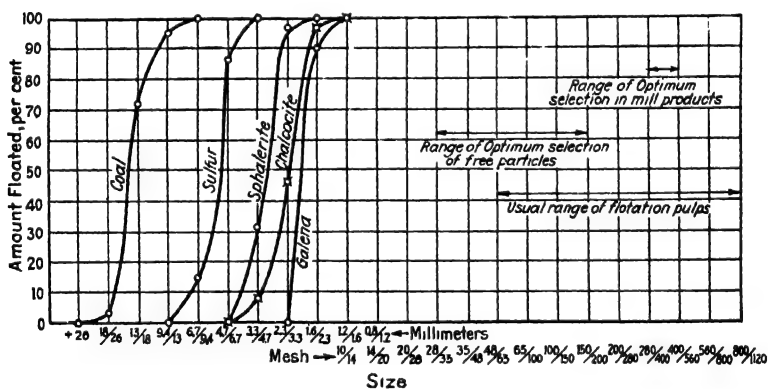


FIG. 35.—Comparative sizes of minerals supported by surface tension.

Data are presented for coal, sulfur, copper-activated sphalerite in xanthate solution, chalcocite in xanthate solution and galena in xanthate solution.

by bubbles into a froth, such a froth could have no permanence unless it were elastic enough to resist such strains as might be placed upon it by coarse, suspended particles. It has already been stated (Chap. V) that the elasticity of bubble films could be ascribed to the lowering in surface tension caused by frother molecules occurring in films in excess of their concentration in the

bulk of the liquid. It is of interest to speculate upon the relationship that might exist between the size of the particles and the difference between the actual surface tension and the surface tension that would exist if the surface had the same concentration of solute molecules as the bulk of the solution. For practical purposes the difference between the surface tensions under consideration is substantially equal to the difference between the surface tensions of pure water and of the frother solution: it is of the order of magnitude of 0.5 to 1.0 dyne per centimeter.

Under the assumption that the effective tension supporting the particles during flotation is the difference in surface tension between pure water and the pulp solution, the supporting tension is but one hundredth, or so, of the total surface tension of the aqueous solution. Accordingly, the maximum size of mineral particles should be of the order of one-tenth of the maximums recorded in Table 25; that is about 0.2 mm. (65 mesh) for galena; 0.3 mm. (48 mesh) for pyrite; 0.5 mm. (30 mesh) for sphalerite and calcite; and 1.3 mm. for coal. These calculated sizes are in good agreement with the effective upper size limits observed in practice.

It is of interest to note that a relationship of the form  $A = K\Delta^m$  in which  $m$  approximates  $\frac{1}{2}$ ,  $K$  is a constant,  $A$  is the diameter of the particles, and  $\Delta$  is the surface-tension depression in dynes per centimeter, was found to fit experimental observations pertaining to the relationship between maximum size of floatable particles and surface-tension depression<sup>(13)</sup>.

The foregoing analysis suggests that a greater amount of frothing agent, up to certain limits, should be used in the treatment of coarser pulps than in that of finer pulps. This is substantiated by the practical fact that a greater amount of frothing agent is used in the flotation of coarsely ground ores than in the treatment of finely ground ores. An example is provided by practice at the Anaconda plant (see Chap. VIII, page 184), where a greater quantity of frother is used in the treatment of the main body of pulp than in the treatment of the slime.



## CHAPTER VIII

### FLOTATION OF SULFIDE ORES OF COPPER

Concentration of the sulfide ores of copper is the largest industrial application of flotation. In many respects it is also the simplest to carry out and the most universally successful. The tonnage of sulfide-copper ores treated annually by flotation is about 70,000,000 tons of which approximately two-thirds is in the United States. The commercial importance of flotation is



FIG. 36.—Flotation floor in the Magna concentrator.

indicated not only by the large scale of the operations (Fig. 36) but also by the fact that fully nine-tenths of the tonnage of sulfide ores of copper is concentrated by flotation instead of being smelted directly, leached, or concentrated by other methods. The improvement resulting from the substitution of flotation for gravity concentration in the treatment of low-grade sulfide-copper ores is typified by the results obtained at the Utah Copper Company<sup>(3)</sup> where mill recoveries were increased from 65 to 90

per cent and the grade of the concentrate substantially bettered by the substitution of flotation for gravity concentration.

### THE PROBLEMS INVOLVED

**Types of Ores.**—In the early days of flotation, copper ores were classified into sulfide and oxidized ores without further regard to the make-up of the ores than the sulfide or oxidized nature of the copper-bearing minerals. In the light of the modern advances in the art it is becoming increasingly desirable to classify sulfide copper ores in accordance with the principal types of mineral associations that are involved.

Broadly speaking, the principal selections to be achieved are of copper-bearing sulfides from silicate minerals, and of copper-bearing sulfides from pyrite. Associations of copper-bearing sulfides with pyrrhotite are relatively scarce, and then they usually involve other valuable sulfides such as pentlandite or millerite (nickel), marmatite (zinc), or galena (lead). In this chapter the study of the sulfide ores of copper is limited to those involving no appreciable quantities of lead, zinc, or nickel. Accordingly the problem of separating copper-bearing sulfides from pyrrhotite is not considered.

Typical ores whose concentration requires primarily the separation of copper-bearing sulfides from silicate minerals are the "disseminated" or "porphyry" ores of the western United States and some schistose ores such as the Roan Antelope ore of Northern Rhodesia. Typical ores involving the separation of copper-bearing sulfides from pyrite and pyrrhotite are the "massive sulfide" deposits. Up to recent times massive sulfide ores have been considered as composed of "cupriferous pyrite" that is of a copper-bearing pyrite. This careless terminology has involuntarily carried the meaning of the existence of copper or copper sulfide as a solid solution in pyrite. Critical study of ores of this type with the microscope has shown that the pyrite does not contain copper in solution but that certain copper-bearing sulfides are very closely associated with pyrite as mechanical mixtures<sup>(13)</sup>.

**Relative Importance of Gangue and Pyrite Elimination.**—In the great majority of sulfide ores the two problems of separating the copper-bearing sulfides from the non-sulfide gangue and from pyrite coexist, although they may be present to a different extent so that they are more or less acutely felt. This is shown by Table

26 in which are given actual plant figures for (a) the ratio of the weight of pyrite to the weight of the copper-bearing sulfides, (b) the ratio of the weight of non-sulfide gangue to that of the copper-bearing sulfides, and (c) the ratio of the weight of non-sulfides to that of sulfides. In Table 26 ores are further classified as disseminated, vein, and massive sulfide ores in accordance with their structure and genesis.

TABLE 26.—RATIOS OF MINERALS TO EACH OTHER IN VARIOUS SULFIDE-COPPER ORES TREATED BY FLOTATION

Type of ore	Plant number	Ratio by weight, pyrite to copper sulfides	Ratio by weight, non-sulfide gangue to copper sulfides	Ratio by weight, non-sulfides to total sulfides
A. Disseminated	1	6.0	26.4	3.7
	2	2.3	9.3	2.8
	3	1.0	38.0	19.0
	4	1.1	7.9	3.8
	5	2.3	31	9.0
	6	3.7	62	13.3
	7	4.0	45	9.0
	Geometric average	2.44	25.1	6.97
B. Vein	8	2.4	10.8	3.2
	9	2.7	8.8	2.3
	10	1.6	9.9	3.8
	Geometric average	2.18	9.8	3.04
	11	6.6	4.7	0.69
C. Massive sulfide	12	8.8	1.4	0.14
	13	11.5	12.5	1.0
	Geometric average	8.75	4.35	0.46

Table 26 shows that the problem of eliminating the non-sulfide gangue from the copper product decreases in importance from disseminated ores to vein deposits and to massive sulfide ores. The table shows also that the problem of eliminating pyrite from the copper concentrate is far more acute for the massive sulfide ores than for disseminated or vein deposits. This



situation is aggravated by the fact that the copper-bearing mineral in high-pyrite copper deposits is chalcopyrite whose copper content is lower than that of the other common copper sulfide minerals, requiring therefore the production of a mineralogically cleaner concentrate.

Considerably greater difficulties have been met in effecting a satisfactory recovery of the copper-bearing minerals as concentrates of adequate grade in massive sulfide ores than in ores in which the gangue is essentially siliceous. Indeed the problem of non-sulfide gangue elimination was the first to be solved industrially, and for some time flotation was applied only to the treatment of disseminated ores.

**Minor Problems.**—Within the scope of the problem of separating sulfides from non-sulfide gangue minerals may be recognized several minor problems of which the most important is that of dealing with micaceous alteration products of feldspars and ferromagnesian minerals. It is not clear whether minerals of this type have a higher floatability in sulfide-floating cycles than feldspars or quartz, or whether their customarily lesser rejection is due to some non-chemical features peculiar to them. Among the non-chemical features, peculiar to minerals having a flaky habit, may be mentioned their breaking to finer particles and their tendency to adhere to the surface of certain sulfides, particularly chalcocite<sup>(13)</sup>. The finer size to which sericite and allied minerals break, together with their flaky shape, raises materially their recovery by overflow in the interbubble water of froths.

Practice has shown that the best way to reduce the fine silicate and aluminous content of sulfide concentrates is to use the smallest amount of frothing agent compatible with suitable operation of the flotation machines, at the same time as a small amount of gangue-dispersing protective colloid such as an alkali silicate, glue, starch, or casein. Double or triple cleaning and the use of a more dilute pulp in the cleaning operations are also helpful.

Elimination of granular silicates is readily obtained and calls for no particular reagents; a limitation of the amount of frother, repetition of the flotation operation on the froth (cleaning), and insurance of adequate liberation of sulfides from silicates are generally sufficient to bring about the desired result.

The separation of copper-bearing sulfides from pyrite and pyrrhotite is much more difficult than that between copper-

bearing sulfides and silicates. It necessitates an understanding of the chemical reaction of these various sulfides to the most diverse pulps.

**The Copper-bearing Sulfides.**—The flotation of sulfide-copper ores differs from that of lead and of zinc ores in that there are a number of sulfide minerals that carry copper, whereas *galena* is the only common lead-bearing sulfide, and *sphalerite* (including *marmatite*) the only zinc-bearing sulfide. The commonest of the copper-bearing sulfides are *chalcopyrite* and *chalcocite*, but *covellite*, *bornite*, *tetrahedrite*, *tennantite*, and *enargite* are not rare; all of these minerals, except *covellite* and *chalcocite*, contain other elements than copper and sulfur: *chalcopyrite* and *bornite* contain iron; *enargite* and *tennantite* contain arsenic; and *tetrahedrite* contains antimony. The presence of various atomic species in the space lattice of these minerals results in differences in their chemical properties, such as differences in polarity, in rates of oxidation, in rates of reaction with collecting agents, in completeness of covering by the collecting agent, in the formation of soluble salts, etc. A good example of the difference in behavior of these minerals is found in the effect of cyanide on *chalcopyrite* and *chalcocite*: *chalcopyrite* is depressed in relatively permanent fashion, but *chalcocite* is depressed only so long as there is some free cyanide ion present, but floats again when the cyanide has been consumed by the mineral.

The various copper-bearing sulfides differ not only in floatability but also in copper content. The production of concentrates that are equally free of non-copper-bearing substances results therefore in products that are widely different in chemical composition, in particular in copper content. Thus, to contain 30 per cent copper, a *chalcopyrite* concentrate containing no other copper-bearing mineral must be 87 per cent pure by weight, whereas a *chalcocite* concentrate need not be over 38 per cent pure. This situation, together with the fact that in most pyritic ores the copper occurs as *chalcopyrite*, has made those ores more difficult to concentrate adequately.

#### SPECIFIC BEHAVIOR OF VARIOUS MINERALS

Data on the behavior of pure *pyrite*<sup>(8)</sup> and pure *chalcocite*<sup>(10)</sup> are available in considerable detail but similar work remains to be done or published for the other sulfide-copper minerals.

**Pyrite.**—Pyrite is extremely floatable if its surface is unoxidized, but the floatability decreases rapidly as surface oxidation is increased. In ores, pyrite is generally more or less oxidized, so that its floatability is not as high as that of the pure mineral, but the extent of its oxidation varies considerably from ore to ore, and from place to place in the same ore body. When using ethyl xanthate as collector the floatability of impure pyrite was found to be increased by the addition of *sodium carbonate*<sup>(8)</sup>. Data as to the pH of the circuit upon the addition of sodium carbonate are not available, but it is likely that the circuit was substantially acid before the addition of sodium carbonate, and approached the range of pH 6.0 to 8.0 on addition of the soda ash.

Pyrite is floated much better through the use of the *higher xanthates* than through that of the lower xanthates; also, it appears to be floated better by xanthates than by mercaptans.

Among the substances that reduce the floatability of pyrite, cyanide (Fig. 39) and lime deserve especial consideration.

Little is known definitely concerning the action of *cyanide*, although it has been claimed that cyanide forms dull coatings upon the otherwise bright surface of the mineral. This assertion is in contradiction with the statements in textbooks on mineralogy concerning the action of cyanide on pyrite and could not be verified<sup>(23)</sup>. Besides the alkaline reaction that cyanide gives to its solutions, the solvent action of cyanide on chalcocite and covellite should be considered as a possible source of decreased floatability for pyrite, having an extremely thin, invisible film of copper sulfide at its surface. Some weight should be attached to this hypothesis, particularly in view of the fact that widely diverging reports concerning the desirability of using cyanide have been received from various quarters. At present it is generally conceded that a small amount of cyanide is desirable to inhibit pyrite in the flotation of most copper ores, and that the amount required is less for massive sulfide ores in which the minerals have been little altered by percolating solutions, than for secondarily enriched disseminated ores where the effect has been proceeding to a greater extent.

The action of *lime* on the sulfides of the United Verde ore (a chalcopyrite-marmatite-pyrite massive sulfide occurring in schist) was studied in detail<sup>(22)</sup>. It was found that all the sulfides, and more particularly pyrite, react with lime to give rise

to soluble sulfides and thiosulfates, which later oxidize to sulfates. These substances may be directly responsible for the inhibition of pyrite by lime. Figure 37 shows that prolonged aeration of fine pyrite in lime solution results in decreased alkalinity, in increased sulfate sulfur in solution (both as calcium sulfate and as sulfuric acid), and in first increasing and later decreasing reducing-sulfur (thiosulfate and sulfide). Whether the same effects as were observed by the staff of the United Verde Copper Company are special to their pyritic ore, or occur with all pyrite, has not been ascertained.

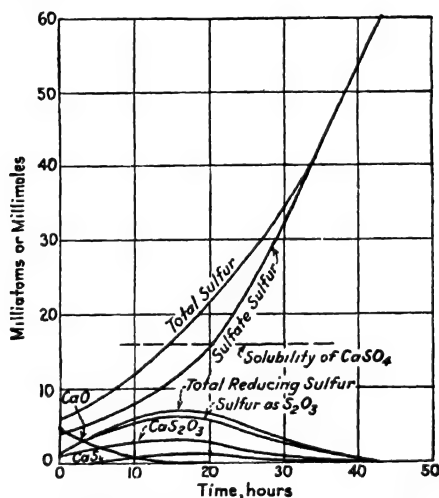


FIG. 37.—Results of prolonged aeration of fine pyrite in lime solution. (After Ralston.)

The effect of pH on the flotation of pyrite is very marked, as can be seen readily by Fig. 38<sup>(7)</sup> in which are compared the effects of additions of sodium hydroxide and hydrochloric acid on the flotation of a pure chalcocite sand and a pure pyrite sand (−200 + 560 mesh), using a critically small quantity of amyl xanthate as the collecting agent. Under the conditions of the experiments pyrite displayed practically no floatability at a pH greater than 7.0.

It is of interest to note that if pyrite and chalcocite are present jointly in a flotation pulp, the results obtained are frequently different from those obtained with the same minerals present singly. This is perhaps a result of the ready oxidation of chalcocite giving rise to a concentration of copper ions in solution

sufficient to activate the pyrite. The useful function of cyanide will be apparent in this connection. The function of alkali, which cyanide combines with its copper-dissolving properties, and which lime displays to a high degree, is useful in limiting the concentration of cupric ions in solution (to that value which obtains on dividing the solubility product of cupric hydroxide by the concentration squared of the hydroxyl ion). The activa-

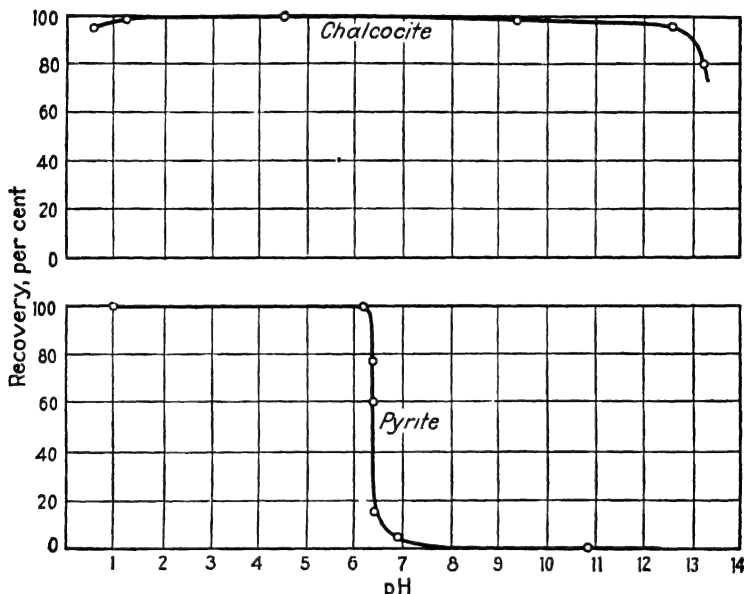


FIG. 38.—Chalcocite and Pyrite.

Relation of recovery to hydrogen-ion concentration. Reagents: terpineol, 0.20 lb. per ton; potassium n-amyl xanthate, 0.03 lb. per ton; NaOH or HCl to suit.

tion of pyrite is, therefore, considerably slower in alkaline circuits than in neutral circuits. In conclusion, it may be considered that an increase in the pH reduces both the floatability of the pure pyrite, and the possibility of its activation by copper salts.

Pyrite that has been inhibited through the use of lime, cyanide, or alkaline circuits may be activated through the use of a soluble sulfide or of an acid (generally sulfuric acid). *Sodium sulfide* is in use at the Midvale plant of the United States Smelting, Mining and Refining Company to float pyrite in the iron circuit; its function may be to sulfidize the oxidized spots at the surface of the mineral. Treatment by *sulfuric acid* is more general than

treatment with a soluble sulfide: the acid appears to remove inhibiting coatings from the surface. The use of acid to cleanse the surface of pyrite may be traced to the earliest applications of flotation. No doubt one of the retarding elements in the introduction of selective flotation has been the extensive use of acid circuits in former days, whereby the surface of pyrite was kept clean of inhibiting coatings.

**Chalcocite.**—The activity of a collector from a homologous series of compounds in floating chalcocite increases as the non-polar part of the reagent molecule increases<sup>(10)</sup>. This conclusion was reached from a study of the behavior of seven *mercaptans*, six *organic sulfides*, seven *organic disulfides*, seven *thiocarbonates* (including *xanthates*), six *thioureas*, nine *amines*, four *hydrazines*, and other miscellaneous reagents. The same conclusion can be drawn<sup>(23)</sup> from a number of experiments carried out on several copper ores including the ores milled at the Anaconda Copper Mining Company's and the Utah Copper Company's concentrators.

One of the most interesting results brought out by the study of the flotation of pure chalcocite<sup>(10)</sup> is that "aliphatic sulfides and disulfides are more active [*as collectors*] than aromatic sulfides and disulfides, although the converse is true of hydrosulfides." This conclusion is in agreement with the results on the selective flotation of copper and lead carbonates which is discussed in Chap. XI and also with certain results concerning the activation of sphalerite by metallic salts<sup>(9)</sup>. It would appear from all these results that aliphatic compounds display greater activity in floating copper minerals, but that aromatic compounds display greater activity in floating lead minerals.

Inhibition of pure chalcocite results, even in the presence of an effective collector, from the addition of small quantities of *thiosulfate*, *sulfite*, *sulfide*, *ferrocyanide*, and *ferricyanide* ions. The action of *cyanide* is worthy of note: cyanide depresses chalcocite completely for a certain period of time after which, the cyanide being all consumed in the formation of cuprocyanide ion, all that is left of its effect is the alkali resulting from its hydrolysis. The inhibiting action of thiosulfate and sulfite ions may be related to the inhibiting action of large amounts of lime, as<sup>(22)</sup> thiosulfate and sulfide ions form by reaction of lime with suspended sulfides. The inhibiting action of ferrocyanide and ferricyanide ions may be due to the dissociation of

these complex ions into cyanide, ferrous, and ferric ions followed by association of the cyanide ion with the copper ion to form the cuprocyanide ion, or to the formation of relatively stable, insoluble polar coatings at the surface of the mineral by reaction of the ferrocyanide and ferricyanide ions with oxidized coatings at the surface of the chalcocite.

**Chalcopyrite.**—Pure chalcopyrite is very readily floated through the use of modern collecting reagents, and even through the use of frothers alone, if its surface is not materially oxidized.

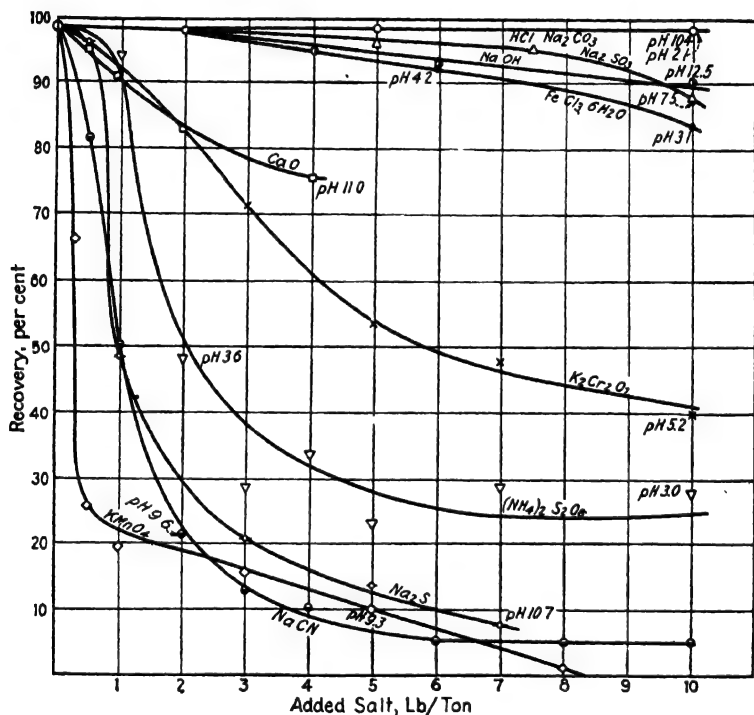


FIG. 39.—Flotation of pure chalcopyrite (100/800 mesh). (Communicated by D. A. Lyon.)

Reagents: terpeneol, 0.20 lb. per ton, with various salts.

Of the copper-bearing sulfides chalcopyrite is perhaps the most refractory to oxidation, so that oxidation frequently halts after proceeding to only a shallow depth, under the same conditions that would result in complete oxidation of other copper-bearing sulfides. The product of oxidation at the surface of

chalcopyrite consists of copper and iron minerals some of which are insoluble in ore solutions. Consequently the chalcopyrite found in ores ranges all the way from the green-gold unoxidized mineral to the reddish-bronze altered mineral. The latter is largely responsible for the losses of copper in the tailings in chalcopyrite-bearing ores.

TABLE 27.—SEPARATION OF CHALCOPYRITE SAND FROM PYRITE SAND USING TERPINEOL (0.2 LB. PER TON) AS THE SOLE REAGENT BESIDES THOSE STATED IN COLUMN 1.

(In the case of each reagent a series of tests was run, but only the test yielding largest selectivity index is recorded.) (After Polisson.)

	Reagent	Quantity, lb. per ton	pH	Recoveries, per cent		Selectivity in- dices in favor of	
				Chalco- pyrite	Pyrite	Chalco- pyrite	Pyrite
A. No sodium silicate	NaOH	2.0	10.2	98.4	38	10	
	CaO	0.16	6.8	80	32	2.9	
	NaCN	0.10	6.3	48	25	1.7	
	Na <sub>2</sub> S	4.0	9.6	19	68	....	2.9
	(NH <sub>4</sub> ) <sub>2</sub> S	4.0	9.6	14.4	71	...	3.8
	Na <sub>2</sub> CO <sub>3</sub>	7.0	9.6	98.6	21	16	
	Na <sub>2</sub> SO <sub>3</sub>	5.0	7.1	93.2	4.4	17	
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	10.0	6.3	93.2	12.0	10	
	Na <sub>2</sub> SnO <sub>3</sub>	5.0	10.5	96	14.0	12.6	
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.0	6.3	81.2	11.6	5.7	
	KMnO <sub>4</sub>	3.0	7.5	71.6	6.4	6.1	
	K <sub>2</sub> CrO <sub>4</sub>	10.0	7.0	92.8	22.0	6.8	
B. With sodium silicate	NaOH	6.0	10.6	87	27	4.2	
	CaO	1.1	10.3	99	7.6	36	
	NaCN	0.5	8.7	89	10	8.5	
	Na <sub>2</sub> S	2.0	9.6	63	92	....	2.5
	Na <sub>2</sub> CO <sub>3</sub>	10.0	9.8	84	49	2.3	
	Na <sub>2</sub> SO <sub>3</sub>	10.0	7.2	88.4	24	4.9	
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	10.0	7.1	80.4	20	4.0	
	Na <sub>2</sub> SnO <sub>3</sub>	10.0	10.8	94	18.4	8.4	
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5.0	5.7	93	12	9.8	
	KMnO <sub>4</sub>	3.0	8.2	89	15.4	6.8	
	K <sub>2</sub> CrO <sub>4</sub>	10.0	7.0	94	60	3.2	
	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.0	6.1	95	38	5.4	
	PbAc	10.0	5.8	88	20	5.5	
	CuCl <sub>2</sub>	5.0	5.2	91	45	3.5	
	HgCl <sub>2</sub>	0.5	6.2	96	35	6.7	



Among the substances which inhibit chalcopyrite must be mentioned *oxidizing agents*, *cyanide ion*, *sulfide ion*, and *lime* (Fig. 39). The action of oxidizing agents seems obvious enough from the foregoing, but the action of cyanide is not clear; it has not been conclusively demonstrated whether the effect of cyanide is related to the formation of insoluble coatings at the surface of the mineral; whether it is due to a wetting of the copper atoms at the surface of the chalcopyrite particles by cyanide ions (which cannot be used up by the mineral on account of its relative insolubility in cyanide); or whether, on the contrary it is caused by a dissolution of surface copper atoms which leave a partly leached iron-bearing surface incapable of reaction with collecting agents.

Table 27 (after Polisson<sup>(20)</sup>) shows the selection obtained between chalcopyrite and pyrite under sundry chemical conditions. In all the tests, terpineol, 0.2 lb. per ton, was the only reagent added besides the variable salts stated in the first column. The minerals were carefully deslimed pure sands (100/800 mesh). Table 27 shows that in circuits, made alkaline with sodium or ammonium sulfide, the chalcopyrite is inhibited but the pyrite is not. Conversely, with all other reagents pyrite is much more readily inhibited. Table 27 shows also that sodium silicate has a beneficial effect on the separation.

In some cases, inhibited chalcopyrite can be reactivated by the use of copper salts.

**Other Copper-bearing Sulfides.**—The floatability of comparatively pure bornite was investigated together with that of chalcocite, chalcopyrite, and pyrite of the same general caliber of purity for certain circuits, now obsolete. The results indicated that bornite is somewhat intermediate between chalcocite and chalcopyrite in its reaction in flotation. Table 28 presents some data obtained on the flotation of bornite from granite in the presence of xanthate, lime, and cyanide.

No data are available concerning the floatability of covellite, but the general results obtained with copper-activated sphalerite are probably largely applicable to the behavior of covellite (Chap. IX).

Table 29 presents data obtained on the flotation of enargite from granite in the presence of xanthate, lime, cyanide, and cyanide followed by copper sulfate.

No data are available concerning the floatability of tetrahedrite or tennantite.

TABLE 28.—FLOTATION OF BORNITE FROM BORNITE-GRANITE MIXTURE

Reagents, lb. per ton			pH	Grade of concentrate, copper, per cent	Copper recovery, per cent	Selectivity index, bornite: silicates
Terpineol	Amyl xanthate	Lime				
0.15	0.02	....	7.3	44.2	82.7	11.8
0.15	0.02	1.5	8.2	40.8	93.6	20.0
0.15	0.02	2.0	9.4	44.6	95.6	23.5
0.15	0.02	3.0	10.5	42.5	97.0	26.9
0.15	0.02	4.5	10.8	47.8	97.0	31.1
0.15	0.02	6.0	11.1	34.7	96.2	18.7
0.15	0.02	8.0	11.4	34.6	95.0	16.3
0.15	0.02	12.0	11.7	33.0	91.8	12.2

TABLE 29.—FLOTATION OF ENARGITE FROM ENARGITE-GRANITE MIXTURES

Reagents, lb. per ton				pH	Grade of concentrate, copper, per cent	Copper recovery, per cent	Selectivity index, copper: silicates
Terpineol	Amyl xanthate	Lime	Sodium cyanide				
0.15	0.01	....	...	7.6	27.6	78.5	8.5
0.15	0.01	1.0	...	8.4	30.3	77.3	9.0
0.15	0.01	1.5	...	8.9	29.7	71.4	7.8
0.15	0.01	2.5	...	10.1	33.3	69.4	9.2
0.15	0.01	3.0	...	10.3	34.7	63.3	9.2
0.15	0.01	6.0	...	11.1	27.1	51.2	5.5
0.15	0.01	9.0	...	11.6	22.1	32.1	3.9
0.15	0.01	12.0	...	11.7	13.8	19.7	2.5
0.25	0.01	1.5	..	8.9	29.7	71.4	7.8
0.25	0.01	1.5	0.1	8.8	32.1	71.8	9.0
0.25	0.01	1.5	0.3	8.7	27.8	53.5	6.0
0.25	0.01	1.5	0.5	10.1	28.3	38.9	5.3

Considering the copper-bearing sulfides as a whole, it may be said that the iron-bearing species resemble pyrite and pyrrhotite in certain ways: they are inhibited by cyanide and by oxidizing agents in alkaline circuits (they can sometimes be reactivated through the use of suitable reagents). Non-iron-bearing copper sulfides are not permanently inhibited by cyanide, whose action lasts only as long as the cyanide has not totally reacted with the mineral and they are relatively unaffected by oxidizing agents.

The inhibiting action of lime is small. Of the two principal iron-bearing copper sulfides, chalcopyrite and bornite, the first is more reluctant to oxidation, as is witnessed by the slower development of tarnish on chalcopyrite than on bornite.

Chalcopyrite is generally a primary mineral, occurring in massive form; chalcocite and covellite are frequently the result of late changes in ore deposition and have the habit of coating the surfaces of other sulfides. As a result they occur in ground pulps as finer particles than chalcopyrite. Greater losses by non-flotation of the very fine particles are therefore more likely to occur in chalcocite-bearing than in chalcopyrite-bearing ores.

Table 30 presents the recoveries of each of the four sulfide copper minerals occurring in the Utah Copper Company ore for each of five sizes, namely +100 mesh, -100 + 150 mesh, -150 + 200 mesh, -200 + 600 mesh, and -600 + 1500 mesh, as calculated from the data presented by H. S. Martin<sup>(13)</sup>, and on the assumption that the over-all sulfide recovery is 91 per cent. (This assumption, even if materially in error, would not change the relative recovery of the four minerals).

TABLE 30.—PERCENTAGE RECOVERY OF EACH COPPER-SULFIDE MINERAL IN THE UTAH COPPER PULP AT EACH SIZE  
(Partly after Martin.)

Mineral	Size, mesh				
	+100	100/150	150/200	200/600	600/1500
Chalcopyrite.....	53	84	90	98.2	94.2
Bornite.. . . .	18	87	91	99.0	93.6
Chalcocite. . . . .	32	77	70	97.1	90.0
Covellite.. . . .	54	92	96	97.5	93.0

**Native Copper.**—The flotation of native copper presents no great difficulties if the ore is properly ground. The malleability of native copper precludes effective crushing. Unless the metal occurs as fine grains in a brittle gangue there is little hope of securing adequate extractions by flotation.

Xanthates are suitable for the collection of native copper, as are mercaptans and dithiophosphates. Maintaining the pH between 7.5 and 8.0 is said to result<sup>(6)</sup> in uniform operative results and in a high recovery of the metal.

**Use of Cyanide in Practice.**—Of the many tests run with ores, a set of data secured by the staff of the American Cyanamid Company<sup>(4)</sup> on Cananea ore is of great interest because of its showing the beneficial value of cyanide in rejecting pyrite. Figure 40 was drawn from calculations based on those data, and on the assumption, otherwise microscopically justified, that about 35 per cent of the copper in Cananea ore occurs as chalcopyrite, 20 per cent as bornite, 15 per cent as covellite, and 30 per cent as chalcocite. This assumption allowed calculation of the recovery of pyrite, and hence the determination of the selectivity index between copper and pyrite rather than between copper and iron. It is only to be regretted that analyses for *sulfide copper* and *oxidized copper* are not available. Figure 40 shows that increasing the cyanide increases the selectivity index, increases the pyrite rejection, and increases the copper recovery up to the addition 1.0 lb. of cyanide per ton of ore. If the cyanide is increased to 1.5 lb. per ton, the copper recovery is decreased considerably, but the selectivity index is again increased.

**Use of Lime in Practice.**—The effect of increasing the amount of lime used in the treatment of a copper-iron ore is well shown by some data presented by A. T. Tye<sup>(26)</sup>. These data (Table 31) were obtained on the same ore (Cananea ore) on which the cyanide comparison (Fig. 40) was made. Besides lime, the reagents used were coal tar and pine oil.

TABLE 31.—EFFECT OF LIME ON THE FLOTATION OF CANANEA ORE  
(After Tye.)

Metallurgical results	Amount of lime, lb. per ton			
	0	1 0	2 0	3 0
Copper recovery, per cent.....	93 4	93.1	93 2	93 3
Iron (as pyrite) rejected, per cent. ....	24	47	60	82.7
Grade of concentrate, Cu, per cent ...	7 6	10 21	11 91	15 31
Grade of concentrate, Fe, per cent.....	34.0	33.4	31 0	19.6
Selectivity index				
Copper to pyrite.....	2 1	3.5	4 6	8.1

Among the many examples of the use of lime in practice the following are of special interest as they relate to ores high in pyrite, that is to ores requiring a good copper-pyrite separation

The first example relates to the treatment of a Canadian copper-iron ore containing approximately 80 per cent pyrite and 7.5 per cent chalcopyrite. Through the use of lime, 10.0 lb. per ton, and of Barrett No. 634 oil, 0.6 lb. per ton, added to

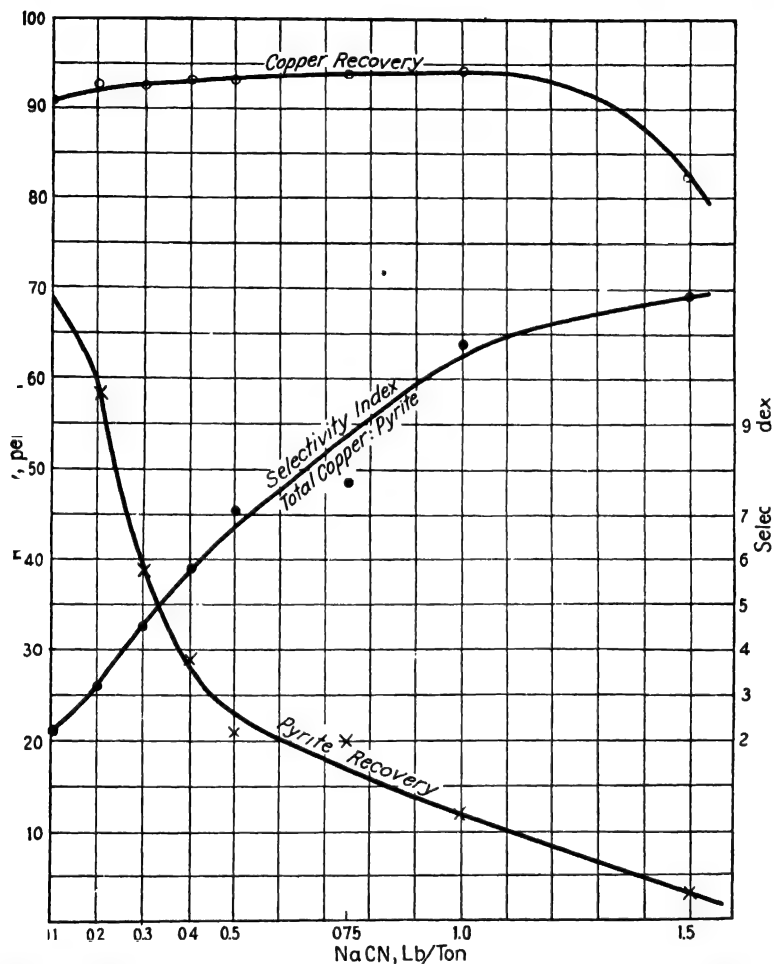


FIG. 40.—Effect of additions of sodium cyanide on the flotation of a pyritic copper ore.

the ball mill, and of T-T mixture (thiocarbanilid dissolved in orthotoluidine), 0.25 lb. per ton, added to the cells, C. S. Parsons<sup>(17)</sup> obtained in a tonnage-scale test a copper recovery of 96.0 per cent with a pyrite rejection of 94.8 per cent; the concentrate contained 22.17 per cent Cu and the tailing 0.12 per

cent, the copper-pyrite selectivity index being remarkably high (21.0).

The second example relates to the operations of the Eustis Copper Company which are described by A. B. Parsons<sup>(18)</sup>. In the treatment of the ore, which contains 59 per cent pyrite and 7.5 per cent chalcopyrite, the use of lime, 11.5 lb. per ton; T-T mixture, 0.31 lb. per ton; and pine oil, 0.022 lb. per ton, results in a copper concentrate assaying 22.1 per cent Cu and containing 91.6 per cent of the total copper; at the same time 94.2 per cent of the pyrite is rejected. In this case, as in the preceding, a large copper-pyrite selectivity index is obtained (13.4).

In these examples, as in the case of the Britannia mill (page 187 this chapter), the copper occurs as chalcopyrite and there is no substantial secondary enrichment which could have activated the pyrite. It is therefore of more than passing interest to note that no cyanide was required. It should be noted, also, that cyanide seems to be required for the treatment of ores in which secondary enrichment has taken place.

#### REAGENT CONSUMPTION

The reagents used in practice in the flotation of copper ores are rather well standardized, the average being approximately as follows (1931):

	Pounds per Ton
Frother (pine oil or cresylic acid) . . . . .	0.12
Collector (xanthate, phosphocresylic acid or thiocarbonyl)	0.06
Pyrite inhibitors:	
cyanide . . . . .	0.05
lime . . . . .	4.00

At average prices for the commodities involved this represents a cost of about 4 cts. per ton of ore. Table 32<sup>(14a)</sup> gives the reagent consumption in the treatment of sulfide-copper ores in the United States (1929). Table 33 gives the reagent consumption in the treatment of sulfide-copper ores from which an iron concentrate as well as a copper concentrate was made (1929).

The extent to which collecting oils are used is more restricted today than in 1929; this is confirmed by the fact that the trend in the replacement of collecting oils by specific chemical collectors for the treatment of copper ores has been displayed over a number of years. The reason for this substitution is the much better

rejection of non-sulfide gangue secured by chemical collectors. This effect is strikingly shown by mill tests on the Consolidated Coppermines ore<sup>(12)</sup> (Table 34) where the use of X-cake (alpha-naphthylamine) 0.15 lb. per ton, and xyloidin 0.10 lb. per ton, in place of coal-tar products, resulted in doubling the copper-silica and copper-alumina selectivity indices, but did not change the copper-iron index.

## PRACTICE

The number of plants at which flotation is used in the concentration of sulfide-copper ores is so large that it would not be possible to discuss all of them, even without details, in the scope of this chapter. It has appeared preferable instead to detail the practice and results at a few plants typical of the various ores that are found. The following plants will be reviewed: (a) the pilot plant of the Roan Antelope Copper Company in Northern Rhodesia, South Africa, (b) the Magna and Arthur plants of the Utah Copper Company at Garfield, Utah, (c) the Anaconda concentrator of the Anaconda Copper Mining Company at Anaconda, Mont., (d) the Miami concentrator of the Miami Copper Company near Globe, Ariz., (e) the Britannia mill of the Britannia Copper Company at Britannia Beach, B. C., Canada, and (f) the Calumet and Hecla Consolidated Copper Mining Company reclamation plant near Houghton, Mich.

This selection has been made to represent as many different types of ores as possible. The Roan Antelope ore body is a high-grade chalcocite deposit with little contaminating sulfides. The Utah Copper deposit typifies disseminated ores with chalcopyrite as the main copper-bearing mineral and a small amount of pyrite as the most objectionable impurity. The Anaconda deposit is typical of vein deposits: it contains chalcocite, enargite, and bornite as the principal copper minerals together with a rather large bulk of pyrite. The Miami ore is a disseminated ore in which chalcocite is the principal copper mineral. In the Miami ore, chalcocite occurs as crusts on pyrite cores. The Britannia ore body is a pyrite-chalcopyrite deposit from which a copper concentrate and an iron concentrate are made. At the Calumet and Hecla Mining Company, flotation is used as a scavenger to reduce the losses of native copper in the five gravity-concentration tailings.

TABLE 32.—REAGENT CONSUMPTION IN THE TREATMENT OF COPPER ORES  
IN THE UNITED STATES IN 1929  
(Treatment of 51,513,791 tons of ore in 36 plants)  
(After Miller and Kidd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
I. Frothers				
Pine oils . . . . .	30	33,315,065	3,996,587	0.120
Cresylic acid . . . . .	8	18,512,839	3,290,354	0.178
Orthotoluidin. . . . .	2	263,862	5,100	0.019
Total frothers. . . . .	34	51,039,985	7,292,041	0.143
II. Collectors				
1. Distillation Products				
Coal-tar creosotes and coal tars. . . . .	5	6,101,943	884,803	0.145
Wood-tar creosotes . . . . .	1	22,858	291	0.013
Petroleum products . . . . .	2	4,029,908	167,655	0.042
Blast-furnace oils . . . . .	3	7,697,886	257,310	0.033
Total. . . . .	9	10,608,729	1,310,059	0.123
2. Synthetic Products				
Xanthates				
Ethyl xanthates . . . . .	29	29,432,863	2,566,352	0.087
Butyl xanthates . . . . .	1	3,609,000	194,252	0.054
Amyl xanthates . . . . .	6	9,672,118	172,672	0.018
Dithiophosphates (aerofloats)				
Dicresyl-dithio- phosphoric acid . . . . .	9	8,768,858	139,011	0.016
Sodium dicresyl- dithiophosphate . . . . .	3	7,322,574	30,240	0.004
Sodium diethyl- dithiophosphate . . . . .	2	17,724,100	308,380	0.017
Benzyl mercaptan . . . . .	1	31,529	650	0.021
Thiocarbanilid . . . . .	2	263,862	1,786	0.007
Total . . . . .	35	51,508,981	3,413,343	0.066
Total collectors . . . . .	36	51,513,791	4,723,402	0.092
III. Acids and Alkalis				
1. Acids . . . . .				
2. Alkalis				
Sodium carbonate . . . . .	1	2,456,304	122,085	0.050
Lime . . . . .	33	51,475,334	215,790,329	4.192
Cement . . . . .	1	576,812	431,987	0.749
Total alkalis. . . . .	33	51,475,334	216,344,401	4.203



TABLE 32.—REAGENT CONSUMPTION IN THE TREATMENT OF COPPER ORES IN THE UNITED STATES IN 1929.—(Continued)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
IV. Other Inorganic Reagents				
1. Sulphidizing				
Sodium sulfide....	3	2,534,652	552,826	0 218
2. Activating.....				
3. Depressing				
Cyanides.....	6	18,694,059	1,057,541	0.057
Trisodium phosphate	2	417,900	18,014	0.043
Total depressing..	7	19,089,101	1,075,555	0.056
4. Miscellaneous Reagents				
Sulfur.....	1	454,020	2,115	0.005
Turpentine .....	2	101,566	2,335	0 023
Total reagents....	36	51,513,791	229,992,675	4.465

TABLE 33.—REAGENT CONSUMPTION IN THE TREATMENT OF COPPER-IRON ORES MAKING TWO CONCENTRATES IN THE UNITED STATES IN 1929  
(Treatment of 481,394 tons of ore in two plants)  
(After Miller and Kidd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
I. Frothers				
Pine oils .....	2	481,394	127,821	0 266
II. Collectors				
1. Distillation Products				
Coal-tar creosotes ..	2	481,394	45,079	0 094
2. Synthetic Products				
Ethyl xanthates ..	2	481,394	105,800	0 220
Dicrosyl-dithiophosphoric acid.....	1	317,497	38,999	0 123
Total.....	2	481,394	144,799	0 301
Total collectors ..	2	481,394	189,878	0 394

TABLE 33.—REAGENT CONSUMPTION IN THE TREATMENT OF COPPER-IRON ORES MAKING TWO CONCENTRATES IN THE UNITED STATES IN 1929.—  
(Continued)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
III. Acids and Alkalis				
1. Acids				
Sulfuric. . . . .	2	481,394	11,816,000	24.545
2. Alkalis				
Lime. . . . .	2	481,394	832,850	1.730
Cement. . . . .	1	317,497	2,640,366	8.316
Total alkalis. . . . .	2	481,394	3,473,216	7.215
IV. Other Inorganic Reagents. . .				
1. Sulfidizing . . . . .				
2. Activating				
Copper sulfate . . . . .	1	317,497	231,300	0.729
3. Depressing. . . . .				
Total reagents . . . . .	2	481,394	15,838,215	32.901

TABLE 34.—RESULTS FROM SUBSTITUTION OF SPECIFIC CHEMICALS FOR OILS AT CONSOLIDATED COPPERMINES COMPANY  
(After Linton.)

Metallurgical results	With coal-tar products	With alpha-naphthylamine and xylidin
Grade of concentrate		
Cu, per cent	13.6	18.3
SiO <sub>2</sub> , per cent.	27.3	13.5
Al <sub>2</sub> O <sub>3</sub> , per cent	7.2	4.5
Fe, per cent . .	20.9	27.6
Average recoveries		
Cu, per cent. . . . .	78	82
Au, per cent. . . . .	53	69
Ag, per cent . . . .	38	40
Fe, per cent . . . . .	41	47
Selectivity indices		
Cu—Fe. . . . .	2.3	2.3
Cu—SiO <sub>2</sub> . . . . .	12.9	22.4
Cu—Al <sub>2</sub> O <sub>3</sub> . . . . .	2.7	5.8

**The Roan Antelope Pilot Plant.**—The Roan Antelope pilot plant<sup>(16)</sup> was operated continuously on the basis of 25 tons per day on a partly silicified shale averaging 3.25 to 3.5 per cent copper, in which the copper occurs principally as chalcocite with varying amounts of bornite. The ore is characterized by the absence of sulfides other than chalcocite and bornite, and by the fine dissemination of the chalcocite in the silicates, requiring grinding to -150 mesh to effect liberation. The treatment of this ore has proved simple, as the only separation to be effected is that of copper sulfides from non-sulfide gangue minerals. The only difficulty seems to arise from the fineness of the gangue particles whose ready overflow tends to pollute the concentrate with silica and alumina.

The flow-sheet consists of a simple roughing-cleaning-recleaning circuit in which the cleaner tailing is returned with the feed to the head of the rougher, and the recleaner tailing with the rougher concentrate to the head of the cleaner. The only reagents required are a frother and a collector, as the ore and the local water are naturally slightly alkaline and the soluble-salt content of the ore is small. The reagent consumption is small: aerofloat, 0.03 lb. per ton; cresylic acid, 0.02 lb. per ton; and pine oil, 0.03 lb. per ton. The reagent cost is therefore about 2 cts. per ton—no doubt one of the lowest on record for a flotation operation. In Table 35 are presented metallurgical data covering the work on four different samples each having been treated over a period of many shifts. The results may therefore be considered similar to those that will be obtained in practice.

TABLE 35.—FLOTATION RESULTS FROM ROAN ANTELOPE ORE  
(After Page.)

	Test 1	Test 2	Test 3	Test 4
Feed, Cu, per cent . . . . .	3.52	3.41	3.39	3.71
Tailing, Cu, per cent . . . . .	0.22	0.207	0.255	0.207
Concentrate, Cu, per cent . . . . .	50.05	55.26	51.08	49.01
Concentrate, Fe, per cent . . . . .	3.49	3.49	3.69	4.63
Concentrate, insoluble, per cent. . . . .	27.9	20.4	25.03	27.46
Concentrate, S, per cent. . . . .	13.45	15.17	14.89	15.13
Calculated recovery, per cent . . . . .	94.10	94.26	92.94	94.32
Calculated ratio of concentration . . . . .	15.1	16.4	16.2	14.0
Cu—insoluble selectivity index. . . . .	28.3	35.0	26.6	28.0

**The Magna and Arthur Mills of the Utah Copper Company.**—These two mills located near Garfield, Utah, are the largest flotation plants in the world, each having a daily capacity of over 35,000 tons of ore (Fig. 36). They can also boast of concentrating at a substantial profit a very low grade ore. The ore consists of a more or less altered granite peppered with grains of sulfide minerals. In order of abundance these minerals are pyrite, chalcopyrite, chalcocite, covellite, and bornite, with pyrite and

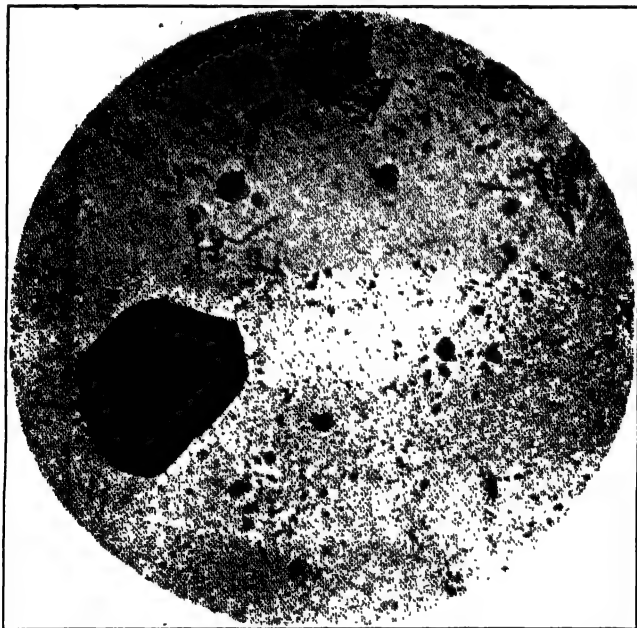


FIG. 41.—Disseminated sulfides in quartz-sericite gangue,  $\times 165$ . (After Martin.)

Portion of quartz-sericite particle about 5 mm. in diameter from Utah Copper ore, briquetted in bakelite and ground to a thin section. The photomicrograph was taken with transmitted light. The sulfides, mostly pyrite, show as black specks in the transparent quartz-sericite gangue. The large black spot is a pyrite grain slightly over 0.1 mm. in diameter; the next largest is under 0.02 mm.; many sulfide specks smaller than 5 microns can be seen.

chalcopyrite much the dominant constituents. The gangue minerals are largely feldspars, alteration products of the feldspars, particularly sericite, and some ferromagnesian minerals. The sulfides are relatively finely associated with each other, and some sulfides occur in close association with certain non-sulfides, requiring fine grinding of the ore for liberation. This may be seen from Figs. 41 to 43<sup>(13)</sup>.



FIG. 42.—Complex bornite-chalcopyrite association,  $\times 290$ . (*After Martin.*)

Bornite containing secondary chalcopyrite veinlets arranged along the crystallographic directions of the bornite. This illustrates the impossibility of liberating completely the copper minerals even by extremely fine grinding. In the pyrite-chalcocite middling particle the intergrowth is not so intimate and would be broken up by slightly finer grinding. Utah copper concentrate (100/150 mesh).

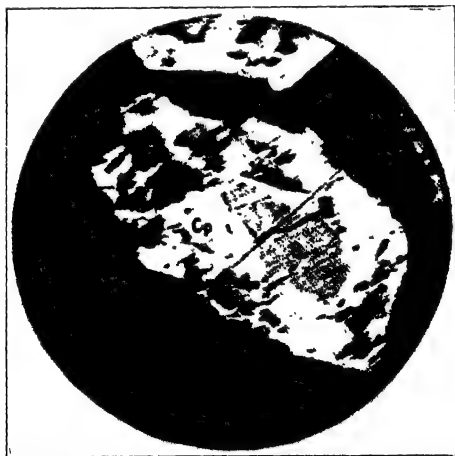


FIG. 43.—Bornite-chalcopyrite-covellite intergrowth,  $\times 290$ . (*After Martin.*)

Particle from Utah Copper concentrate (100/150 mesh). Center is core of bornite about 35 microns thick containing minute secondary veinlets of chalcopyrite, surrounded by rim of chalcopyrite about 30 microns thick, which in turn is encased in a thin shell of covellite from 7 to 10 microns thick. Black spots are polishing pits in the surface of the minerals.

The flotation division of the flow-sheet is very simple; it consists of a roughing step followed by two cleaning steps, with the tailing of the rougher cells discarded, the tailing from the first cleaners returned at the head of the roughers, and the tailing from the recleaners returned at the head of the cleaners. At the Magna mill (Fig. 44), the pulp is divided by distributors ① into several sections; in each section the roughing machine ② is composed of eight cells each, the concentrate of which proceeds

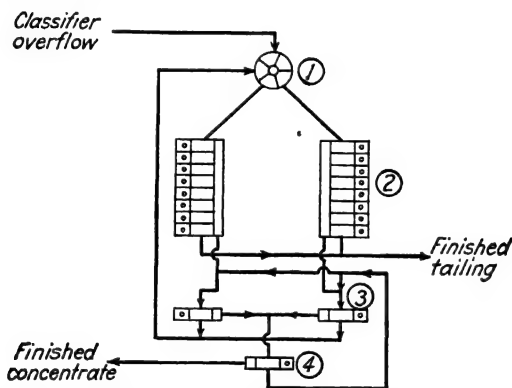


FIG. 44.—Unit in flotation division at Magna concentrator.  
Each unit consists of two sections.

to one cleaning cell ③; the concentrate from the cleaning cells of two sections is recleaned in one recleaner ④. Thus for each recleaner there are two cleaners and 16 roughers. The machines in use at the Utah Copper Company were designed by T. A. Janney of the Company's staff and feature a combination of agitation and pneumatic introduction of air. They are known as Janney mechanical-air machines (Chap. XIV).

The reagents employed have varied from year to year as improvements were introduced. As collectors the following in turn have proved satisfactory in an experimental way: xanthates, mercaptans, and dithiophosphates (cresyl, ethyl, butyl, and amyl). At present a very small amount of sodium butyl or sodium amyl dithiophosphate is used; the amount used approximates 0.015 lb. per ton. As a frother, cresylic acid (about 0.05 to 0.10 lb. per ton) has been found superior to pine oil as it results in a concentrate containing less non-sulfides. A small amount of cyanide (about 0.07 lb. per ton) has been found necessary as an adjunct to lime for inhibiting pyrite. Lime is the main pyrite

depressant and gives an alkaline circuit. The amount of lime is regulated to give a pH of 8.6 to 9.0, a higher amount of lime than that giving a pH of 9.0 resulting in substantial copper losses, although the grade of the concentrate is improved. The amount of lime varies as the soluble-salt content of the ore varies; 4 to 6 lb. per ton is usually required. The reagents are added at the head of the cells, except the lime which is added in the ball mills and the cyanide which, at the Arthur plant, is added to the thickeners which happened to be available and are now used as surge tanks between the classifier overflow and the flotation cells.

TABLE 36.—METALLURGICAL RESULTS AT UTAH COPPER PLANTS (1929)  
(Partly after Engelmann<sup>(5)</sup>)

Feed, copper, per cent. . . . .	0.98
Feed, iron (largely as pyrite), per cent. . . . .	2 5
Concentrate, copper, per cent. . . . .	32
Concentrate, iron, per cent. . . . .	30
Tailing, copper, per cent. . . . .	0 10
Recovery, copper, per cent. . . . .	89.5
Selectivity index, copper to non-sulfide gangue, about. . . . .	60
Selectivity index, copper minerals to pyrite, about. . . . .	7

The reagent cost at the Utah Copper Company plants is under 4 cts. per ton of ore treated, lime being the largest item.

**The Anaconda Copper Concentrator<sup>(15)</sup>.**—The Anaconda copper concentrator located at Anaconda, Mont., is one of the largest in the world, treating up to 15,000 tons daily of a relatively high-grade ore.

The Anaconda ore is a vein-copper ore in which the valuable copper minerals are characterized by their variety. The principal copper minerals are chalcocite, bornite, and enargite, but varying quantities of covellite, tetrahedrite, tennantite, and chalcopyrite also occur. About one-third of the copper is present in minerals containing also some arsenic, and principally as enargite. Considerable silver occurs (about 0.5 to 0.7 oz. for each 20 lb. of copper), but its particular occurrence is not quantitatively known. It is probable that, like copper, it occurs in a variety of forms and that part of it is in the form of some arsenic-bearing mineral. The ore contains a large amount of pyrite (15 to 25 per cent by weight on the ore), but as the copper content of the ore is high, the pyrite content may be considered as relatively moderate. Besides the sulfides, the ore

contains silicate minerals particularly feldspars, alteration products of the feldspars, such as sericite, and quartz.

From a flotation standpoint the problems that require solution are the prevention of collection of the micaceous alteration products of the feldspars and inhibition of pyrite.

In view of the high grade of the feed, and of the high copper content of the copper-bearing minerals, a high-grade concentrate should be readily obtainable. The grade of the concentrate, however, is lower than in many plants operating on a lower grade feed. This is said not to be the result of inability to raise the grade of the concentrate with the Anaconda ore, but rather a limitation set by the smelting of an arsenic-bearing concentrate; if the grade of the concentrate were raised, the arsenic content in it would be raised, making the smelting of the concentrate a more difficult operation. Also, raising the grade of the concentrate to 35 or 40 per cent copper would result in a slightly reduced recovery which would fully balance the slight overvaluation of the copper in the concentrate resulting from raising the grade above 25 per cent Cu.

In Fig. 45 are presented (a) the flow-sheet of each of the flotation sections for the body of the pulp (except the section milled by gravity concentration for the production of sulfuric acid); and (b) the flow-sheet for the "primary slime." The primary slime is removed from the ore after the completion of the intermediate crushing and just ahead of the fine grinding section through the use of conical classifiers of the Anaconda type (Chap. VII, Fig. 26). The main body of the pulp is treated in seven sections.

The pulp of each section, after desliming, is ground in ball mills in closed circuit with Dorr classifiers, then delivered to a five-way distributor ① which sends the pulp to five 15-cell sub-aeration M.S. flotation machines, each cell being 3 ft. square, and fitted with a 21-in. impeller ②. A finished concentrate is taken from the first five cells and a middling from the last ten. The middling is returned at the head of the first cell; the tailing is discarded, and the concentrate is sent to the dewatering plant.

The treatment of the primary slime is more complicated than that of the main body of the pulp; upon its discharge from the Anaconda classifiers the primary slime is too thin to be floated; it is therefore thickened in 40 batteries of four 28- by 3-ft. Dorr thickeners ③ to a pulp consistency of 20 per cent solids. The thickened pulp is split by distributors ④ and conditioned in



12 batteries, each consisting of 15 M.S. agitators (5). Following this conditioning, the pulp is combined again and fed by a divider (6) and two four-way distributors (7) to eight double primary Callow flotation machines having ten 3- by 3-ft. pans

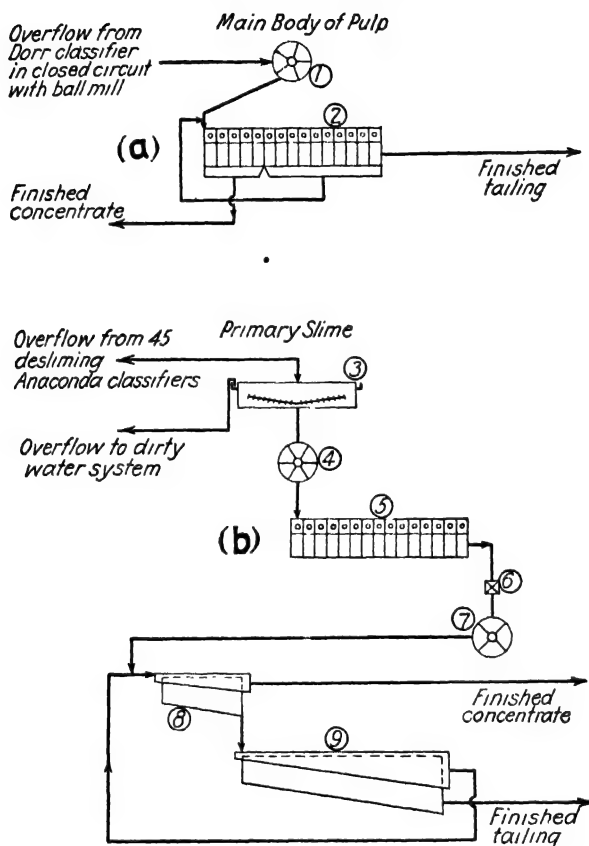


FIG. 45.—Unit in flotation division at Anaconda.

(a) Section of flow-sheet for main body of pulp. (b) Section of flow-sheet for slime plant.

each, (8). These Callow cells make a finished concentrate and a primary tailing which is treated further in eight double Callow flotation machines having forty-four 3- by 3-ft. pans each, (9). The concentrate from these scavenging cells is sent to the head of the primary cells (8) and the tailing is discarded.

Until recently the reagents used in the treatment of the Anaconda ore have been a combination of sodium ethyl xanthate,

lime, and pine oil. More recently some dithiophosphates have been used in an experimental way. A small amount of coal-tar oil is also used. Table 37 indicates the reagents used.

TABLE 37.—FLOTATION REAGENTS USED AT ANACONDA COPPER CONCENTRATOR, POUNDS PER TON OF FEED  
(After Morrow.)

Reagents	At mill treating main body of pulp	At slime plant
Burned lime . . . . .	5 7	5 8
Steam-distilled pine oil . . . . .	0.15	0 04
Destructively distilled pine oil . .		0.04
Coal-tar oil . . . . .	0 08	
Xanthate . . . . .	0 10	0.25

Table 38 shows strikingly that metallurgical results are much better in the treatment of the main body of the pulp than in the treatment of the primary slime. This is in accordance with the data presented in Chap. VII on the behavior of very finely ground pulps.

TABLE 38.—MILL PERFORMANCE AT ANACONDA  
(After Morrow.)

Metallurgical results	Main plant	Slime plant
Grade of feed, copper, per cent . .	3.97	4 16
Grade of feed, iron, per cent . . .	14 8	5.8
Grade of concentrate, copper, per cent	29 6	20 3
Grade of concentrate, iron, per cent	20.2	19.7
Grade of tailing, copper, per cent . .	0 24	0.40
Recovery, copper, per cent . . . . .	95 0	92.0
Recovery, iron, per cent . . . . .	20.8	64.2
Selectivity indices		
Cu-Fe . . . . .	8 5	2 5
Cu-SiO <sub>2</sub> . . . . .	36.4	14 8
Cu-Al <sub>2</sub> O <sub>3</sub> . . . . .	24.2	13 2

Proper alkalinity control is maintained by titration of the pulp solution for free lime. Titrations are carried out with standard sulfuric acid solution, and the indicator used is phenolphthalein. In current operations the pH of the tailing water is maintained at about 12.0 by keeping a titratable amount of lime of 0.5 to

0.7 lb. per ton of tailing water. Colorimetric tailing assays are made at hourly intervals and the operators vary the amount of xanthate according to the copper assay. The colorimetric tailing assays, obtained through the use of ammonia, check the assays obtained by laboratory analysis within 0.03 per cent.

**The Miami Concentrator.**—The Miami concentrator of the Miami Copper Company is located near Globe, Ariz., and treats an average of 12,000 tons daily of what is probably the lowest grade copper ore that is now milled. The ore averages 0.86 per cent copper of which approximately 0.10 per cent is oxidized.

The Miami ore is characterized by the presence of chalcocite as crusts at the surface of pyrite. This makes the separation of the two minerals a difficult matter from a structural standpoint. Also, if complete liberation of the ore minerals should be effected, the cost of crushing and grinding would be very high in view of the low grade of the ore. The relatively low crushing cost currently attained results from the use of two grinding circuits. In the primary grinding circuit the sulfides are liberated from the silicate gangue, but the liberation of the sulfides from each other is very incomplete. A collective concentrate containing the sulfides is produced after the primary grinding. This concentrate is ground finer and refloats to separate the chalcocite from the pyrite.

The flotation and regrinding divisions of the flow-sheet are shown in Fig. 46. The mill is divided in six units, the fine grinding sections of each unit consisting of ball mills in closed circuit with bowl classifiers. The overflow from each of the bowl classifiers goes to a mechanical-agitation flotation machine ① consisting of 32 cells; thence to a similar 16-cell scavenging flotation machine ② which makes a finished tailing; the concentrate from ② is fed back to ① and the concentrate from ① is cleaned in one eight-cell machine ③ whose tailing is returned to ① and whose concentrate is the collective concentrate for retreatment.

The collective concentrate from the six sections is mixed and goes to a Dorr classifier ④ for desanding before thickening. Thickening is accomplished by three 40-ft. Dorr thickeners arranged in series, two ⑤ being used for the first step and one ⑥ for the second. The overflow from ⑥ is sent to the reclaimed-water system. The underflow from ⑤ and ⑥ and the sand from

④ are ground in a ball mill ⑦ in closed circuit with a Dorr bowl classifier ⑧, which overflows into a Hunt flotation machine ⑨ making a finished copper concentrate and a high-grade tailing. This tailing is treated in ⑩ to yield a middling concentrate which is returned to ④ and a middling tailing which is given a further opportunity to float in a 14-cell sub-aeration machine ⑪.

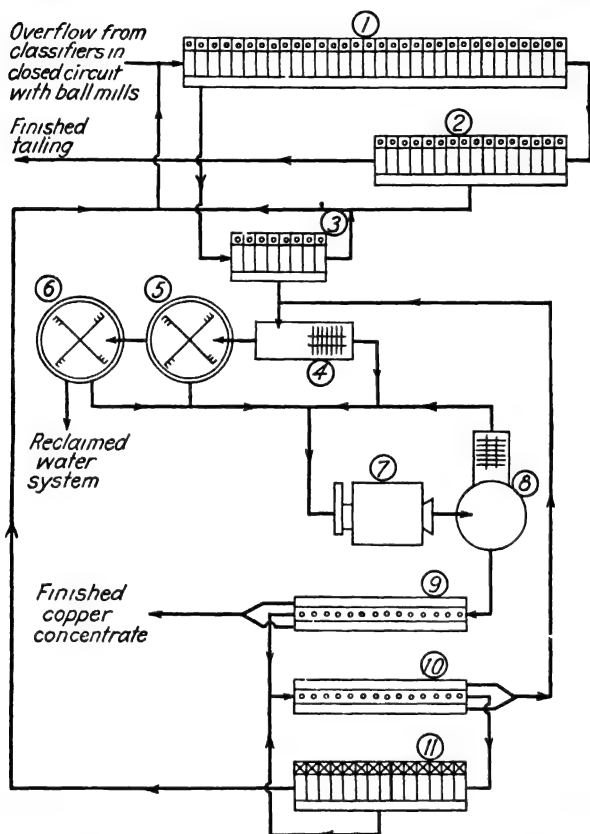


FIG. 46.—Flotation and regrinding divisions of one unit at Miami concentrator.

The sub-aeration machine yields a froth which is returned to ⑩, and a tailing which is returned, with the primary grinding-mill discharge to one of the section feeds.

The reagents used at Miami are substantially standard, consisting of lime, 2.1 lb. per ton; potassium ethyl xanthate, 0.07 lb. per ton; and pine oil, 0.15 lb. per ton. The lime is added in part to the ball mills, in part to the fresh and reclaimed water,

and in part to the classifiers of the retreatment plant. Water reclaiming, such as is obtained through the use of a large tailing thickener, has resulted in reduced pine-oil and lime consumption.

Metallurgical results are approximately as follows (Table 39).

TABLE 39.—METALLURGICAL RESULTS AT THE MIAMI CONCENTRATOR (1929)

Mill feed, copper, per cent . . . . .	0 86
Mill feed, sulfide copper, per cent. . . . .	0 76
Mill feed, oxidized copper, per cent. . . . .	0. 10
Primary concentrate, copper, per cent. . . . .	19
Primary (finished) tailing, copper, per cent. . . . .	0.10
Retreatment concentrate, copper, per cent. . . . .	40
Retreatment tailing returned to head of primary flotation, copper, per cent. . . . .	6
Recovery, total copper, per cent. . . . .	87
Recovery, sulfide copper, per cent . . . . .	93
Recovery, oxidized copper, per cent . . . . .	40

**The Britannia Mill<sup>(19)</sup>.**—The Britannia Mining and Smelting Company has been treating daily by flotation 4000 tons of a pyritic copper ore at Britannia Beach, B. C. The ore consists of chalcopyrite and pyrite “in a hard quartz porphyry gangue, which is often changed to a quartz-mica-schist spotted with films of chlorite.” The valuable constituents in the ore are chalcopyrite, with which is associated some silver, pyrite which is recovered in a concentrate of low copper content, and is used for the manufacture of sulfuric acid, and gold which occurs partially in the free state.

The Britannia flow-sheet embodies the principle of separate flotation of the primary slime which is used also at the Anaconda plant (Fig. 45). The Britannia flow-sheet embodies as well the principle of first grinding the ore enough to reject the silicate gangue without completely inhibiting the pyrite, and of grinding the collective concentrate before refloating it selectively: this scheme is used also at the Miami plant (Fig. 46). Figure 47 presents the flow-sheet of the flotation division of the Britannia plant: ① is a 21-cell standard spitz-type M. S. flotation machine used in the separate flotation of the primary slime of the ore which has been separated from the granular portion of the pulp ahead of the fine-grinding section; ② represents one 21-cell and three 14-cell standard M. S. machines used in parallel in floating collectively the remainder of the pulp. The concentrate

produced from ① and from ② averages 9 to 11 per cent copper. In the condition in which it is after removal from the roughing cells, the collective concentrate cannot be segregated into a copper product and a pyrite product without regrinding because

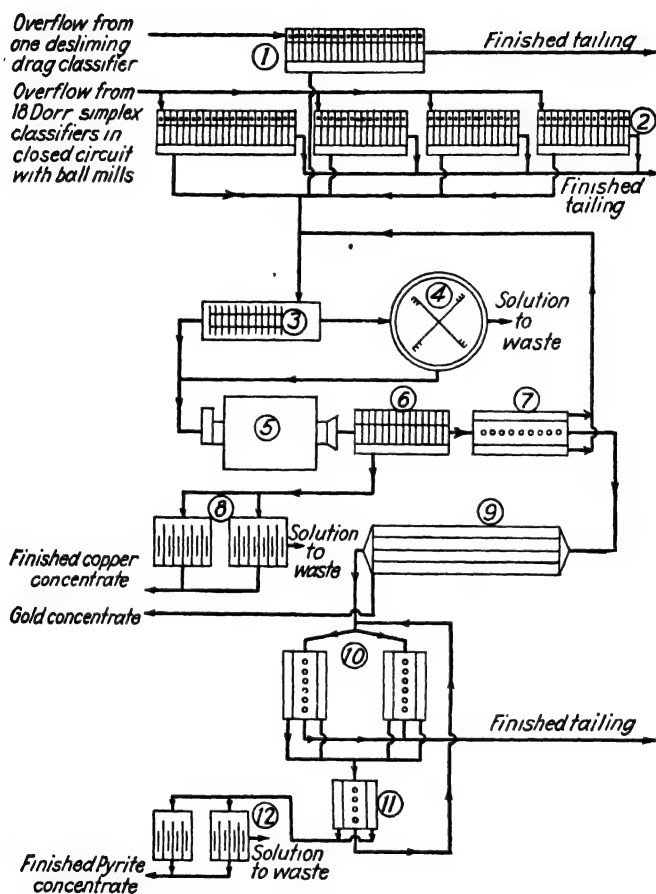


FIG. 47.—Flotation and regrinding division at Britannia concentrator.

a large portion of the particles are still locked. They could of course have been liberated before the collective flotation operation, but this would have involved considerable expense for the grinding of a large tonnage of barren, hard, siliceous material. In view of the cost of this grinding operation, and of the small increased recovery of the metals that it would bring, it was

considered advisable by the metallurgical staff to sacrifice the simplified flow-sheet to economy in crushing expenditure.

The retreatment operation is perhaps the most interesting phase of the practice at Britannia. The rougher concentrate is first classified by a drag classifier (3) into sand sent to a 7- by 12-ft. ball mill charged with 1-in. balls (5) and slime sent to a 44-ft. Dorr thickener (4). The thickener underflow is directed to the same mill to which the classifier sand is sent. Thus, the first step in the retreatment is to remove excess water from the concentrate, and with it some of the reagents in the collective concentrate; if all the reagents gathered in the collective concentrate were allowed to proceed to the retreatment section metallurgical results would be adversely affected because an excess of some reagents would be present. After regrinding and addition of the proper reagents, the rougher concentrate is floated selectively in a 14-cell M. S. machine (6), the concentrate being a finished product that is dewatered directly in two six-leaf, 8-ft.-diameter, American filters (8). The tailing from (6) is floated in a Forrester scavenger cell (7) which reduces the copper content of the pulp from 3 to 0.25 per cent. The concentrate obtained in the Forrester cell is returned to the drag classifier (3) for regrinding.

Up to recently (1927) treatment of the pulp stopped at this stage; it was found however that considerable gold escaped in the pyritic retreatment tailing, and that a part of this gold was in the free state; it was also found that due to the advantageous position of Britannia's operations near the ocean, a pyrite concentrate could be made and sold at a profit for the manufacture of sulfuric acid. Such a situation might not arise with mining operations located at a substantial distance inland, because the returns from the sale of pyrite concentrate would be consumed by freight charges.

The gold is recovered by passing the pyritic tailing of the retreatment plant on a series of blanket-covered launders (9) inclined at a slope of about 1.5 in. per foot, then washing the launders every 8 hr. to collect the gold particles that accumulate on the blankets. The pyrite is recovered by flotation, the usual combination of roughing (10) and cleaning (11) flow-sheet being used. The pyrite concentrate is dewatered directly in two four-leaf, 6-ft. American filters (12).

Table 40 presents the metallurgical data for June, 1927.

TABLE 40.—METALLURGICAL RESULTS AT THE BRITANNIA  
CONCENTRATOR (1927)  
(After Pearse.)

Copper concentrate	•
Copper, per cent . . . . .	20 5
Iron, per cent . . . . .	29 0
Insoluble, per cent . . . . .	6.2
Composite tailing	
Copper, per cent . . . . .	0.15
Iron, per cent . . . . .	3.2
Ratio of concentration	13.6
Gold recovery, per cent	62.3
Silver recovery, per cent	75.3
Copper recovery, per cent	91 3

Table 41 summarizes the use of reagents in the mill circuits.

TABLE 41.—REAGENTS USED AT BRITANNIA MILL  
(After Pearse.)

Place of addition	Reagents							
	Alkaline reagents		Frothers		Collectors			
	Soda ash	Lime	Pine oil	Fumol	Coal tar	Canadian hard-wood creosote	Xanthate (K-ethyl)	Sodium resinate
I Roughing*								
a Primary slime ahead of flotation at cells . . .	8 0		0.15	0.05	..	..	0 25	
b Main body of pulp at ball mills ahead of cells at middle of cells		0 8	0 15 0 10	.. ..	0 12	0 03	0 03 0 02	0 005
II Retreatment								
a Flotation of copper† at ball mills at cells		1 75	0 02					
b Flotation of iron‡ ahead of cells at cells			0 40		....	...	0.30	

\* Reagents stated in pounds per ton of ore

† Reagents stated in pounds per ton of rougher concentrate

‡ Reagents stated in pounds per ton of pyrite concentrate



Some notable features deserve especial consideration: (a) the use of soda ash in the primary slime circuit as contrasted with the use of lime in the main body of pulp; (b) the comparatively small lime requirement; (c) the comparatively large requirement for frothers; (d) the disparity in the amount of xanthate needed in the primary slime circuit and in the main body of pulp; and (e) the judiciously selected place of addition for the various reagents.

Pearse<sup>(19)</sup> says that soda ash is used in place of lime in the primary slime circuit to precipitate the soluble salts of the ore that have become concentrated in that circuit by the desliming operation, because soda ash does not flocculate the pulp whereas lime does; in this way losses of mineral by occlusion in flocs is eliminated. Also, since a large amount of alkaline reagents has to be used in the treatment of the slime, the danger of using a substantial excess is more marked than in the treatment of the granular pulp; since an excess of soda ash may not lead to any more disastrous results than a waste of reagent, whereas lime might inhibit the flotation of chalcopyrite if used in excess, the use of the costlier soda ash is preferred to that of the dangerous lime.

The lime requirement in the granular pulp is small, both in the roughing and in the retreatment steps; this is partly because of the removal of soluble salts from the circuit by segregation of the pulp into primary slime and granular pulp, and partly because in the primary flotation operation it is not desired to make more than a crude separation of the pyrite from the chalcopyrite.

The comparatively large requirement for frothers is probably the result of the coarse condition of the pulp. This is indicated by the desirability of reducing the frother content of the pulp before retreatment and is partly responsible for the thickening of the rougher concentrate before retreatment.

The disparity between the amount of collector required for the primary slime and for the granular pulp is common to the majority of the plants treating separately their sand and their slime. It is caused by two factors: (a) the greater extent to which oxidation of sulfides exists in the particles of primary slime and (b), the greater fineness of the sulfides in the primary slime which has a larger surface on which collector action is necessary.

Oily collectors and sodium resinate were retained as recently as 1927 to toughen the froth. It is not known whether these reagents are still in use.

Careful attention to the place of addition of the reagents is nowhere more evident than at Britannia. This is illustrated by the following features: (a) alkaline reagents are added at the grinding mills to afford more extensive action between them and the surfaces of the minerals to be inhibited and to give fuller opportunity to the lime to go in solution and precipitate the soluble salts; (b) frothers are added at the cells; and (c) addition of the collector is made at the cells either in "teaspoon" quantities at the points at which it is desired to exert some selective action between sulfides having a different floatability, or else in such a way as to provide contact with the pulp where no selective action but complete collection is desired. In this connection it may be noted that Ruggles and Adams<sup>(21)</sup> find no improvement in copper recovery, but a distinct lowering of the grade of the concentrate if the collector (xanthate or thiocarbamid) is added at the ball mill instead of at the flotation cell (Inspiration ore). Some of their results are presented in Table 42.

TABLE 42.—EFFECT OF PLACE OF ADDITION OF COLLECTOR ON METALLURGICAL RESULTS AT INSPIRATION  
(After Ruggles and Adams.)

Point of addition	T-T mixture				Potassium ethyl xanthate	
	Flotation cells		Ball mill		Flotation cells	Ball mill
Number of days, mill run . . . .	31	29	26	36	12	4
Grade of concentrate, per cent copper . . . . .	34.7	36.5	29.4	30.8	35.8	30.4
Grade of concentrate, per cent insoluble . . . . .	13.2	11.6	16.8	12.7	10.9	22.1
Grade of concentrate, per cent iron . . . . .	20.1	19.9	21.9	22.4	20.0	18.5

The cost for flotation reagents at Britannia is about 4.5 cts. per ton, the total flotation cost being 7.5 cts., exclusive of patent royalties. Dewatering and storage add 1.5 cts. per ton to the cost given above. In 1927, the total milling cost including all

steps from primary crushing to filtering, including overhead charges and royalties, was 42.6 cts. per ton.

**Lake Superior Practice**<sup>(6)(1)(11)</sup>.—The native copper ores of the Lake Superior region are of two types: amygdaloid and conglomerate. In the amygdaloid ores the copper occurs as relatively coarse fillings in vugs, and it is almost completely liberated at 48 mesh; liberated particles of copper are generally flattened by the crushing action. In the conglomerate ores the copper is finely disseminated and crushing to 200 mesh is necessary for effective liberation.

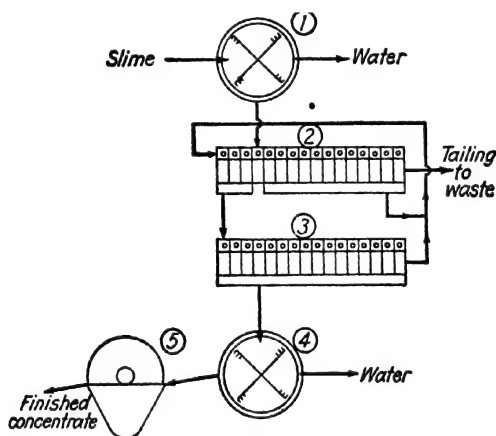


FIG. 48.—Flotation division at Calumet and Hecla concentrator.

Flotation is now used in the treatment of both the conglomerate and amygdaloid ores. The following description<sup>(27)</sup> applies to the treatment of the conglomerate ores of the Calumet and Hecla Consolidated Copper Company. The finest portion of the pulp (roughly -200 mesh) is thickened (Fig. 48) so the dilution is 25 per cent solids in 12 four-compartment Dorr thickeners (1), then floated in four 24-in., 16-cell M.S. Standard flotation machines (2). The thickened pulp from (1) goes to the fourth cell of (2) which is used as a conditioning or mixing cell; a rougher concentrate is drawn from the last 12 cells of (2) and sent to the first cell for cleaning, a cleaned concentrate being drawn from the first three cells. The cleaner concentrate from the four M.S. machines is re-cleaned in one re-cleaner (3) whose tailing is returned at the head of (2). The cleaned concentrate is thickened (4) and filtered in an 8- by 8-ft. Oliver filter (5).

On account of the relatively high silicate content, the filter cake contains a large amount of moisture, 14 per cent. Reagents used are sodium ethyl xanthate, pine oil, and soda ash. The reagent cost is less than 4 cts. per ton treated.

Metallurgical results are approximately as given in Table 43.

TABLE 43.—METALLURGICAL RESULTS AT CALUMET AND HECLA  
NATIVE-COPPER FLOTATION PLANT

(After *Weinig and Palmer.*)

Grade of feed, per cent Cu .....	0.50
Grade of tailing, per cent Cu.. .....	0.09
Grade of concentrate, per cent Cu.....	35.0
Selectivity index, Cu: all gangue.. .....	25.0

Fahrenwald<sup>(17)</sup> recommends the use of a pH of 7.5 to 8.0 for best results and claims that control of the pH within these limits is best obtained with sodium dibasic phosphate; pH control can also be obtained with lime or soda ash.



## CHAPTER IX

### THE FLOTATION OF SULFIDE LEAD-ZINC ORES

The flotation of sulfide-lead and sulfide-zinc ores is best considered together because sulfide lead-zinc ores are more common than straight-lead or straight-zinc ores; indeed lead-zinc ores are far more common than was realized a few years ago, when no economical method for concentrating them was known. Lead-zinc ores generally contain varying amounts of iron, some copper, silver and gold. The presence of iron is an objectionable complication which materially affects the grade of the products that can be obtained. If copper, silver, and gold are sufficiently abundant the expenditure of substantial efforts to collect them in that product which gives these metals the greatest economic value is justified.

Until 1920 little headway was made in the treatment by flotation of lead-zinc ores but since that time progress has been continuous in the separation of the two metals from each other as well as in the securing of higher recoveries and cleaner concentrates.

The progress that has been accomplished in this line is well illustrated by Table 44 which presents the results obtained from

TABLE 44 — YEARLY METALLURGICAL RESULTS AT MORNING MILL

Year	Lead concentrate		Zinc concentrate		Recoveries in lead concentrate		Recoveries in zinc concentrate		Selectivity index Pb: Zn in lead circuit
	Pb, per cent	Zn, per cent	Pb, per cent	Zn, per cent	Pb, per cent	Zn, per cent	Pb, per cent	Zn, per cent	
1921	44.6	12.2	6.6	44.7	76.3	39.2			2.2
1922	44.9	13.7	6.4	46.1	73.7	35.6	1.1	13.0	2.3
1923	44.9	13.0	6.9	43.9	79.6	40.4	1.6	18.3	2.4
1924	50.7	12.4	8.3	40.5	78.5	35.6	4.9	44.1	2.6
1925	58.4	11.4	7.1	42.5	83.9	27.5	4.7	47.4	3.7
1926	63.1	8.3	4.7	48.6	85.8	18.4	4.0	66.8	5.2
1927	65.5	8.2	3.2	50.4	88.8	16.9	3.1	74.5	6.3
1928	71.3	6.6	3.6	49.6	90.3	13.1	3.7	81.2	7.9
1930 (est.)	(75)	(5)	2.7	57.0	(92)	(8)	3.1	86.5	(11.5)

year to year at the Morning mill of the Federal Mining and Smelting Company, Mullan, Idaho.

The success of flotation in producing two marketable concentrates out of complex lead-zinc ores, which previously had to be smelted in lead blast furnaces and were penalized for their zinc content, has been largely responsible for an improved status of the mining industry in many camps; it has also led to favorable consideration of flotation as an ore-treatment method in other fields of application. The flotation of lead-zinc ores is now standardized and fool-proof. As a more perfect separation of lead from zinc obtained, the use of flotation in the treatment of lead-zinc ores has expanded, so that ores which formerly were treated to make one concentrate only now are beneficiated by selective flotation to recover separately the metal occurring in minor amount.

At the present time over 15,000,000 tons of lead, zinc, and lead-zinc ores are treated annually by flotation. Half of this is milled in the United States.

**The Minerals in Lead-zinc Ores.**—The commoner minerals occurring in sulfide-lead, zinc, and lead-zinc ores include galena, sphalerite and marmatite, pyrite and pyrrhotite as the essential sulfides; quartz, feldspars, micas, pyroxenes, hornblendes, calcite, dolomite, siderite, rhodochrosite, barite, sericite, chlorite, graphite, garnet, and epidote as the principal non-sulfide gangue minerals.

Scarcer constituents of lead-zinc ores are jamesonite (a lead-antimony sulfide), bournonite (a lead-copper sulfide), and minor quantities of copper-bearing sulfides, particularly tetrahedrite, tennantite, and chalcopyrite. The silver content of lead-zinc ores is generally one of its most valuable constituents. Silver occurs in a variety of forms generally associated with lead and copper.

In some ores the sulfide content is so high, to the exclusion of non-sulfide gangue, that the ore may be considered as approximating a matte in appearance and structure. Frequently the texture of aggregates of the sulfides of lead, zinc, and iron is fine, at the same time that the texture of the sulfide-non-sulfide aggregate is relatively coarse. The non-sulfide gangue varies considerably. Depending upon the country rock, the gangue may be composed of the minerals of an altered granite, of typical vein minerals such as barite or rhodochrosite, of quartzite, of

crystallized or graphitic limestone. Ores having a substantial proportion of carbonates in the gangue are typified by the restrictions in pulp pH imposed by the carbonates.

### FLOTATION OF PURE MINERALS

**Galena.**—Pure, unoxidized galena floats readily without the addition of a collecting agent, a frother alone being required. This can be ascertained by grinding pure galena particles in water under anaërobic conditions, and floating immediately. An

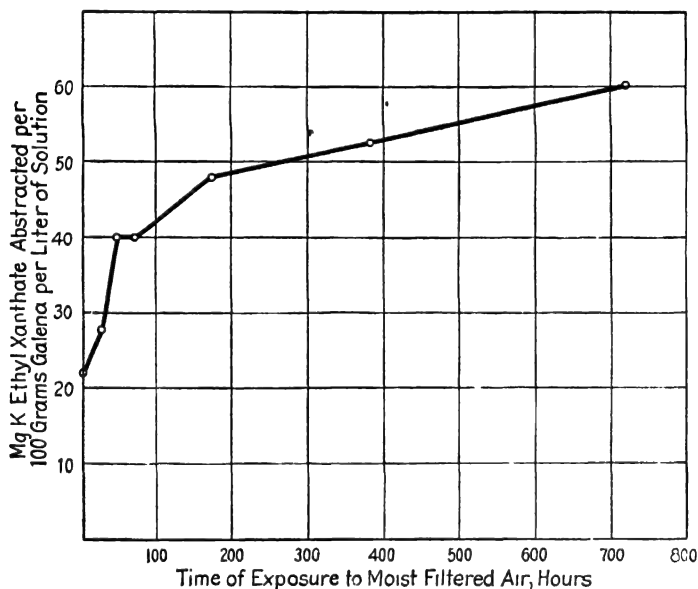


FIG. 49.—Oxidation of galena as gauged by the removal of potassium ethyl xanthate. (After Taggart, Taylor and Knoll.)

alternative method consists in first leaching a deslimed galena sand with a solvent for basic lead sulphate, such as ammonium acetate, and washing with air-free water before floating.

In practice galena particles are more or less oxidized during grinding and classification, requiring varying amounts of collecting agent to yield satisfactory extractions. This is illustrated by some experimental data obtained on  $-100 + 800$  mesh galena sands (Table 45).

Figure 49 shows the abstraction of potassium ethyl xanthate from solution by dry-ground galena exposed to moist air for varying lengths of time. It shows that the xanthate abstraction



TABLE 45.—AMOUNT OF COLLECTOR (AMYL XANTHATE) REQUIRED WITH 0.10 LB. TERPINEOL PER TON AT PH 8.5 TO 9.0 (MADE ALKALINE WITH SODIUM CARBONATE) TO YIELD 90 TO 92 PER CENT EXTRACTION OF GALENA FROM A CHARGE OF PURE DESLIMED MINERAL

Condition of Mineral	Xanthate, Lb. per Ton
1. Dried on a hot plate.....	0.14
2. Dried under a hot plate.....	0.095
3. Dried on blotting paper.....	0.043
4. Dried on blotting paper and leached once with 5 per cent ammonium acetate for 10 min. at 50°C. then washed six times in air-free distilled water.....	0.021
5. Same as 4, except that saturated ammonium acetate is used and the solution was boiled.....	0.008

which Taggart, Taylor, and Knoll correlate with extent of surface oxidation increases at a slackening rate with duration of exposure to oxidizing agencies.

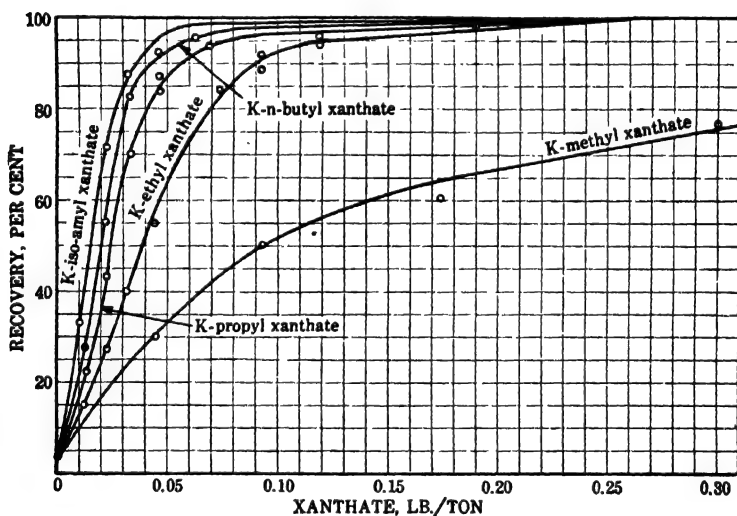


FIG. 50.—Galena.

Flotation of 100/600-mesh particles with terpineol, 0.10 lb. per ton,  $\text{Na}_2\text{CO}_3$ , 1.0 lb. per ton, and xanthates as shown.

Taggart, Taylor, and Ince<sup>(22)</sup>, determined, for coarse galena particles, the magnitude of a certain index which is said to parallel the collectability of the mineral. This index depends upon (a) the angle of contact between the gas-liquid and the solid-liquid interfaces of a gas bubble adhering to the surface of the submerged mineral particles, and (b) upon the relative distortion of

TABLE 46.—EFFECTIVENESS OF REAGENTS AS COLLECTORS FOR GALENA AS PREDICTED FROM THE DATA OF TAGGART, TAYLOR, AND INCE (A. I. M. M. E., *Tech. Pub.* 204.)

Collecting ability*	Name of reagent	Quantity used in tests, † parts per million parts of water
A.....	Thiocresol	40
	(Ethyl) xanthic anhydride	25
	Amyl xanthate	25
B.....	Lead (ethyl) xanthate	25
	Potassium (ethyl) xanthate	25
	Thiocarbanilid	50
	Amyl disulfide	50
	Azo-naphthalene	40
C.....	Sodium dithiophenyl carbamate	40
	Thiophenol	50
	Tolucno-azo resorcinol	40
	Xanthic acid	250
	Xanthogenamide	25
	Azo-benzene	250
	Carbothialdin	375
	Diazo-amino-benzene	100
	Dixanthogen	25
	Ethyl methyl xanthate	250
D.....	Alpha-naphthylamine	25
	Beta-naphthylamine	50
	Phenylhydrazine	50
	Phenyl thiourea	25
	Phenyl thiourethane	25
	Amyl mercaptan	50
E.....	Ditolyl thiourea	25
	Heptyl mercaptan	50
	Ethyl ethyl xanthate	250
F.....	Heptyl sulfide	50
	Mercapto-benzo-thiazole	25
	Ortho-toluidine	100
	Benzidine	50
O.....	Cresol	25
	Thiourea	125
	Xylidine	50

\* The classification of collecting ability into the classes A, B, C, D, E, F, O corresponds to values of Taggart, Taylor, and Ince's relative collecting index of above 110, 90-110, 70-90, 50-70, 30-50, 10-30, under 10, respectively. Potassium ethyl xanthate was chosen arbitrarily as having a relative collecting index of 100.

† This quantity of reagent was dispersed in water by agitation in a square glass jar with a revolving impeller; the suspension was then filtered through infusorial earth and allowed to act on a coarse particle of mineral.

the bubble at rupture. From the data of Taggart,<sup>1</sup> Taylor, and Ince it may be estimated *qualitatively* that the collecting ability of various collectors for galena is as shown by Table 46. The data of Taggart, Taylor, and Ince indicate that thiophenols, more particularly thiocresol, xanthic anhydride, and xanthates are the best collectors for galena, but that mercaptans and their oxidation products, as well as dixanthogen (an oxidation product of ethyl xanthate) are not so effective.

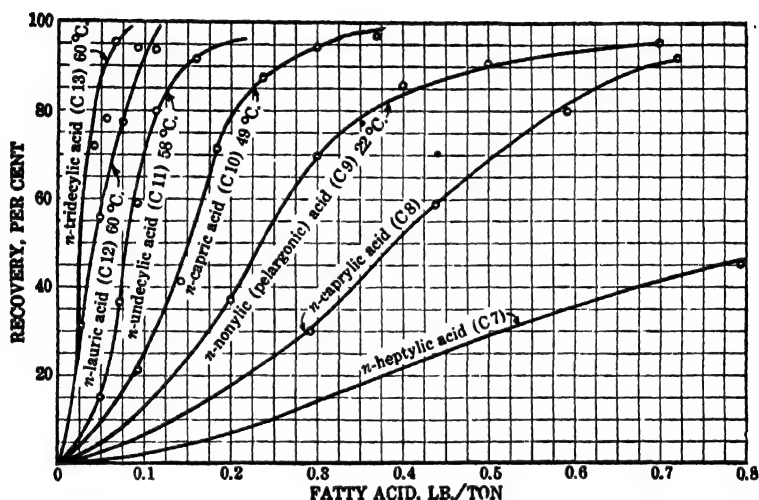


FIG. 51.—Galena.

Flotation of 100/600-mesh particles with saturated fatty acids and terpeneol, 0.40 lb. per ton.

The effect on the recovery of deslimed, slightly oxidized, but otherwise pure galena caused by xanthates having various hydrocarbon chains is shown by Fig. 50<sup>(8)</sup>. The marked increase in recovery with increased length of the hydrocarbon chain should be noted.

Figure 51 shows the effect caused by various fatty acids of the paraffin series. The promoting effect of increased length in the hydrocarbon chain is again evident. It is interesting to note that the amount of galena recovered with fatty acids is dependent upon the temperature, decreasing sharply as the temperature decreases below the melting point of the fatty acid. This result is perhaps to be correlated with the observation that metallurgical results in the treatment of non-metallic and oxidized

minerals with fatty acids and soaps are improved by heating the pulp.

The effect of additions of salts to galena pulps was studied under two different sets of conditions: (a) using potassium xanthate as the collector<sup>(8)</sup>; and (b) using eucalyptus oil<sup>(24)</sup>. The accord in the results is worthy of note in view of the differences in experimental conditions: in one case the galena was deslimed and dried before floating and in the other case the galena was

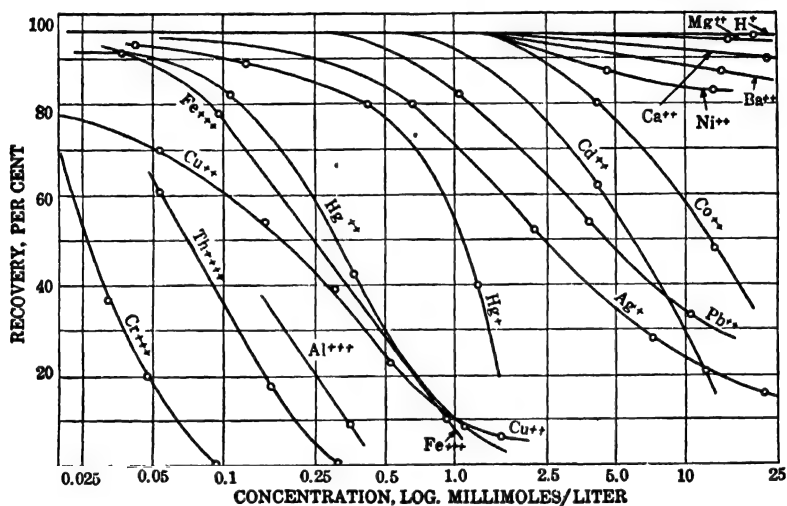


FIG. 52. —Galena.

Effect of cations (as nitrates) on the flotation of 100/600-mesh particles with terpincol, 0.20 lb. per ton, and potassium ethyl xanthate, 0.10 lb. per ton.

ground dry and not deslimed; the reagents used were terpincol and potassium ethyl xanthate in one case and eucalyptus oil in the other. The experiments showed that various cations have marked inhibiting properties toward galena and that the toxicity of the various cations increases with the valence of the cation. Figure 52 illustrates this point. Table 47 correlates the toxic effect of cations with the insolubility of the base-metal sulfides formed by these cations.

Galena particles having somewhat oxidized surfaces (that is, particles filmed with a sulfate, basic sulfate, or carbonate skin) are readily inhibited by a number of salts which form lead salts less soluble than the coating and less soluble than the lead salt of the chemical collector used. Inhibiting agents of that sort are chromates, phosphates, tungstates, arsenates, and arsenites.

TABLE 47.—SOLUBILITY OF SULFIDES AND TOXIC ACTION OF CATIONS  
(After Taylor and Bull.)

Data from Gaudin using xanthate	Data from Taylor and Bull using eucalyptus oil	Solubility of sulfide, mols per liter
Ag (most toxic)	Ag (most toxic)	$\text{Ag}_2\text{S}, 0.52 \times 10^{-6}$
Pb	Pb	$\text{PbS}, 1.21 \times 10^{-6}$
Cd	Cd	$\text{CdS}, 9.0 \times 10^{-6}$
Co	Ni	$\text{NiS}, 39.62 \times 10^{-6}$
Ni	Co	$\text{CoS}, 41.62 \times 10^{-6}$

Fresh galena particles are inhibited by the same salts provided they can first be oxidized. For this reason the dichromate ion is

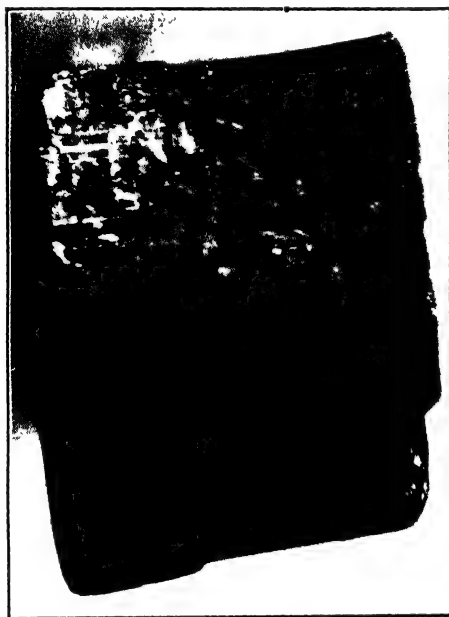


FIG. 53.—Action of acid potassium dichromate on fresh galena,  $\times 10$ .

Solution contained 600 parts of potassium dichromate and 1000 parts of sulfuric acid per million parts of water. Reaction time, 15 min. Upper half of particle was protected by paraffin coating.

particularly effective. Visible coatings are produced by potassium dichromate on galena in sulfuric acid circuits even if the concentration of the dichromate is as low as 0.005 per cent (Fig. 53). These coatings are quite white in circuits having a high sulfate-ion concentration, but distinctly yellow if little sulfuric acid has

been used. <sup>1</sup>Fresh galena is not tarnished by chromates, even if the chromate is present in relatively high concentration (of the order of 0.2 per cent), or if the reaction is allowed to proceed overnight at room temperature at a pH over 8 or under 11.

The antagonism in the actions of potassium dichromate and potassium xanthate on galena having a slightly oxidized surface is shown by Fig. 54. The dichromate and xanthate ions are competing for reaction with the basic sulfate at the surface of the mineral

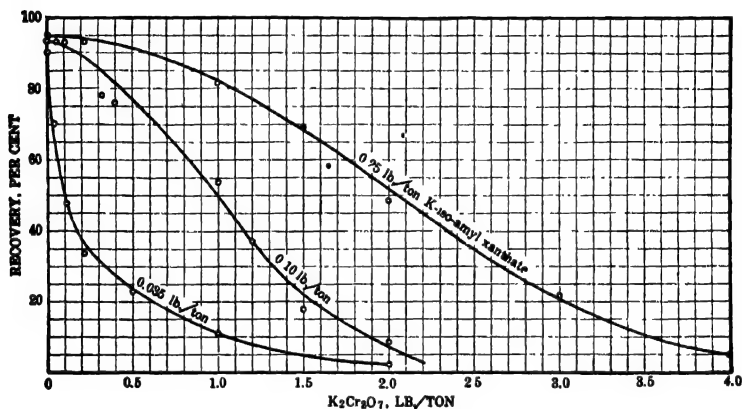


FIG. 54.—Galena.

Flotation of 100/600-mesh particles with terpineol, 0.10 lb. per ton, and various amounts of potassium-iso-amyl xanthate and potassium dichromate as shown.

to form insoluble lead salts, one of which is polar and the other non-polar in the direction in which its molecules face the water.

Lime has been reported as harmful to the flotation of galena; however, plant experience indicates that unless very large quantities are used, there is no marked inhibition.

The effect of the pH on the flotation of galena has not been definitely ascertained but it appears as though there is a relatively wide band of pH values through which galena is readily floatable with the usual reagents.

**Sphalerite.**—Broadly, the flotative properties of sphalerite(9) (10) (16) (20) (21) are as follows:

1. Pure sphalerite is one of the most difficultly floatable of the sulfides. Organic compounds whose hydrocarbon groups contain less than five carbon atoms usually do not collect the mineral unless used in very large amount. Thus, pure sphalerite is less floatable than pure chalcocite, chalcopyrite, pyrite, or galena.

2. The hydrogen-ion concentration of the pulp is a very important factor in the flotation of unactivated sphalerite. With several collectors, for instance, a satisfactory recovery can be obtained only by control of the pH within narrow limits.

3. Few collectors are known for unactivated sphalerite that do not also collect non-sulfide minerals. The most powerful are di-iso-amyl ammonium di-iso-amyl dithiocarbamate; xanthates

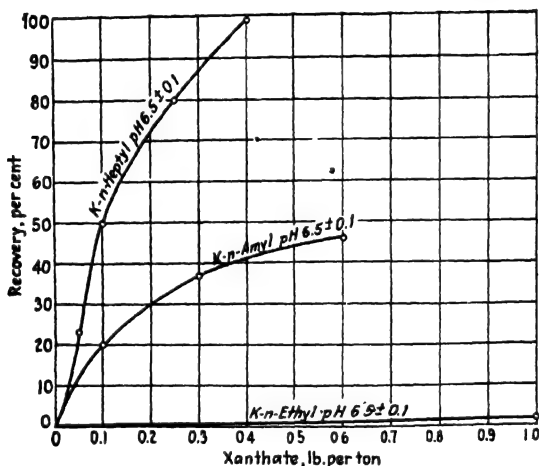


FIG. 55. —Sphalerite.

Flotation of 100/600-mesh particles, using various xanthates as collectors.

higher than hexyl xanthate, trithiocarbonates higher than propyl trithiocarbonate, certain amines, and certain hydrazines.

4. Relatively coarse pure sphalerite does not abstract ethyl xanthate from solution and is not floated thereby (Fig. 55).

5. Sphalerite is very amenable to activation by salts of the metals whose sulfides are less soluble in water than zinc sulfide. These activators include silver, copper, mercury, cadmium, and lead salts.

6. Sphalerite acquires readily from copper-bearing solutions a coating of covellite having a thickness of a few atomic diameters; thereafter the reaction is slow; however, visible coatings of covellite can be prepared at high temperature and identified as such. Figure 56 shows a coating of covellite formed by copper sulfate at the surface of sphalerite, one section of which has been removed by leaching with potassium cyanide.

7. Covellite-plated sphalerite abstracts xanthates from solution and is floated thereby.

8. The covellite coating of sphalerite previously treated with copper sulfate solutions is readily dissolved by cyanide solutions owing to the formation of the substantially undissociated complex cupro-cyanide ion,  $\text{Cu}(\text{CN})_3^-$ .<sup>1</sup> Cyanide solutions have therefore a cleansing action on sphalerite surfaces.

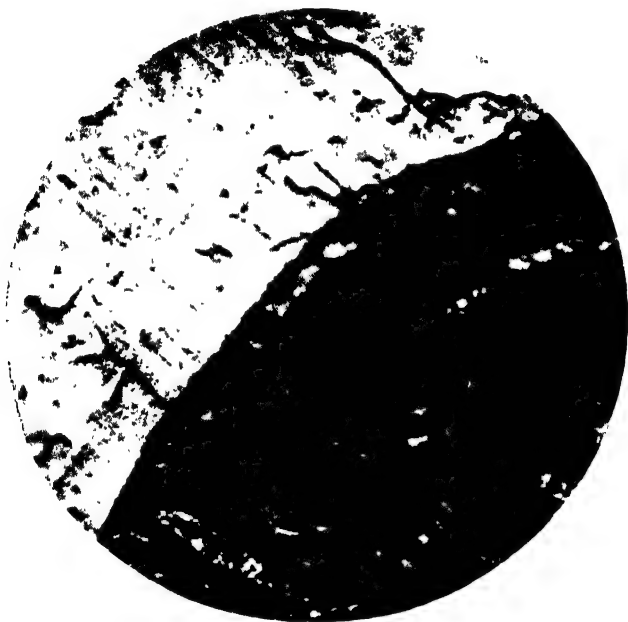
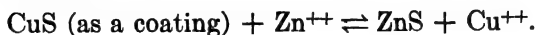


FIG. 56.—Sphalerite coated with covellite as the result of treatment with copper sulfate,  $\times 44$ .

9. Cyanide solutions greatly decrease the floatability of copper-activated sphalerite, bringing it back to the normal floatability of pure sphalerite which is very slight with ethyl xanthate.

10. Zinc salts assist cyanides in reducing the floatability of sphalerite by supplying zinc ions to take the place of the copper atoms at the surface of the  $\text{ZnS}$  lattice, and by driving to the right the reaction:



<sup>1</sup> In a  $N/1000$  cyanide solution the ratio  $\frac{[\text{Cu}^{++}]}{[\text{Cu}(\text{CN})_3^-]}$  is of the order of  $10^{-30}$  according to W. D. Bonner and Sol G. Ravitz<sup>(1)</sup>.



11. Naturally occurring zinc ores contain sphalerite in various stages of activation by copper salts (sometimes silver salts, too, Fig. 24) and therefore call for the use of various amounts of cyanide and zinc sulfate to inhibit, and of copper sulfate to activate the zinc mineral.

12. The sequence of potency of the various activators for sphalerite, namely copper, silver, mercury, cadmium, and lead salts, is not the same for all collectors but rather depends upon the insolubility of the salt formed by the anion of the collector with the cation of the activating salt, as well as upon the insolubility of the sulfide coating upon the sphalerite.

The action of soluble sulfites on the flotation of sphalerite was discussed by R. A. Pallanch<sup>(18)</sup>. Pallanch considers that the separation of galena from sphalerite by the use of soluble sulfites results from the formation of coatings of zinc sulfite at the surface of the sphalerite, and from the non-formation of similar coatings at the surface of the galena. In certain pH ranges the formation of complex cuprosulfite ions may play an important part, as does the formation of complex cuprocyanide ions in the case of the use of cyanides.

Sodium sulfide has been claimed effective in depressing sphalerite while at the same time not depressing galena or pyrite<sup>(13)</sup>. This inhibiting agent could therefore be used to advantage where it is desired to float jointly the galena and the pyrite. Table 48 illustrates the effect of sodium sulfide on a pyrite-sphalerite-galena ore.

TABLE 48.—DATA ON HELLSTRAND PROCESS  
(After Taggart.)

Reagents: commercial sodium sulfide, 4.0 lb. per ton; coal-tar creosote, 0.225 lb. per ton; pine oil, 0.025 lb. per ton.

Product	Grades			Recoveries		
	Pb, per cent	Zn, per cent	Fe, per cent	Pb, per cent	Zn, per cent	Fe, per cent
Feed.. . . .	2 02	16 2	1 7			
Lead concentrate	22 3	13 1	19 6	78 4	5 8	82.8

Universal practice is to activate sphalerite with copper sulfate before floating. From the foregoing it is clear that the properties

of sphalerite after activation are much the same as those of cupric sulfide. It is not surprising, therefore, to find that the organic hydrosulfides, particularly alkyl mercaptans, are very good collectors for sphalerite, just as they are for copper sulfides and carbonates. Indeed, the use of hydrosulfides in place of xanthates for the collection of copper-activated sphalerite sometimes permits the production of cleaner concentrates, if considerable pyrite is present (Table 49).

TABLE 49.—COMPARATIVE EFFECTS OF POTASSIUM ETHYL XANTHATE AND OF AMYL MERCAPTAN IN FLOATING BLEND FROM A HIGH-IRON ZINC ORE HAVING A PYRITIC GANGUE

Metallurgical data	Test 1	Test 2	Test 3
Reagents, lb. per ton			
Lime.....	2 0	2.0	4.0
Copper sulfate.....	0 75	0.75	0.75
K-ethyl xanthate.....	0.10		
Amyl mercaptan.....		0.08	0 08
pH of tailing solution.....	10.8	10.6	12.2
Zinc content, per cent			
Feed.....	4.3	4.3	4.3
Concentrate.....	30 5	41.2	47.3
Tailing.....	1.05	0.35	0 50
Iron content, per cent			
Feed.....	12 6	12.6	12.6
Concentrate.....	24.4	15.1	8.3
Tailing.....	11 4	12 1	13.1
Zinc recovery, per cent.....	78	92	89
Iron recovery, per cent.....	21	12	5
Selectivity index, zinc: iron.....	3.7	9.2	12.4

The reaction of copper sulfate with sphalerite is rapid unless the pH is high (say over 11), in which case it is delayed due to the low cupric-ion concentration that is imposed by the high hydroxyl-ion concentration (mass action effect of  $[\text{Cu}^{++}]$  and  $[\text{OH}^-]$  on the dissociation of  $\text{Cu}[\text{OH}]_2$ ). In some instances it is therefore desirable to condition the pulp, that is to allow a substantial time for reaction after the copper sulfate has been added and before flotation. In practice this is done in a variety of ways, particularly through the installation of conditioning tanks.

#### THE PROBLEMS IN THE TREATMENT OF LEAD-ZINC ORES

The problems that arise in the treatment of complex lead-zinc ores may be classified as follows:

1. The separation of lead and zinc sulfides, occurring singly, from the associated non-sulfide gangue.
2. The separation of lead-bearing sulfides from zinc-bearing sulfides.
3. The prevention of iron sulfides from floating with the lead and zinc sulfides. This is particularly important in the zinc-floating cycle.
4. The collection of the copper, silver, and gold minerals.

**Separation of the Sulfides from Non-sulfide Gangue.**—The separation of galena or sphalerite from associated gangue is very simple and high selectivity indices (ranging from 30 to 100) may be expected if the gangue is granular (siliceous or carbonate).

If the gangue is micaceous, clayey, or sericitic the production of a clean concentrate is difficult as the fine light flakes of mica or sericite and the clay particles overflow readily in the concentrate with interbubble water. The best way to reduce the collection of fine gangue minerals in the concentrate involves a combination of chemical and mechanical ways: wetting of silicates is promoted by sodium carbonate and sodium silicate, and their mechanical overflow in the concentrates is minimized by repetition of the cleaning steps and by the use of more dilute pulps particularly in the cleaners and recleaners. The recovery of fine gangue in the lead or zinc concentrate can also be cut down by reducing the fine-gangue content of the pulp through desliming before fine grinding. Where the gangue is carbonaceous its elimination from the concentrates is difficult. This is due both to the flakiness and to the non-polar character of the graphitic material. This problem has been acutely felt in the treatment of certain lead and lead-zinc ores. No definite solution to the difficulties has been found. In those plants making two or three base-metal concentrates the problem of serious gangue interference is substantially limited to the lead-floating cycle because it is customary to float the lead minerals first.

The presence of a high carbonate content in the gangue is a favorable factor as it compels the pulp to be slightly alkaline and therefore disposes of soluble salts without the necessity of using large quantities of alkaline reagents to precipitate them.

**The Lead-zinc Separation.**—The separation of lead sulfides from zinc sulfides is relatively simple but it has required considerable effort on the part of those engaged in industrial research

to bring it about, and on the part of scientific investigators to determine its causes and establish its limitations. Although the problems arising from the efforts to separate lead from zinc sulfides are not fully solved, they are sufficiently well understood to constitute no great practical difficulty.

Four general methods have been proposed to separate galena from sphalerite and marmatite. These methods are based on the use of (a) cyanide with or without zinc sulfate; (b) sodium sulfide; (c) a soluble sulfite or sulfurous acid with or without zinc sulfate; and (d) a chromate or dichromate with or without copper sulfate. Of these methods the first three aim at permitting the galena to float while inhibiting the sphalerite. The last method is aimed at inhibiting the galena while floating the sphalerite. The cyanide-zinc-sulfate method is the most widely used.

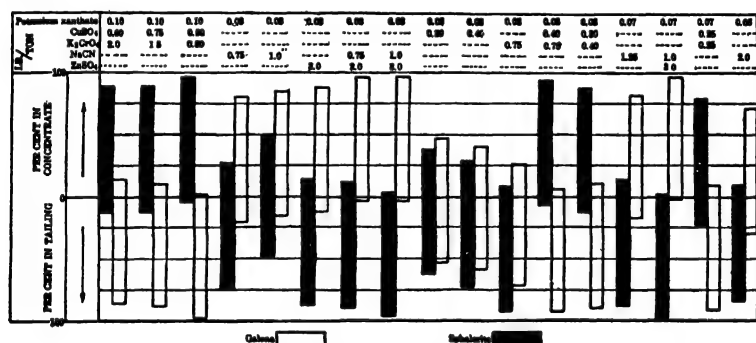


FIG. 57.—Differential flotation of galena-sphalerite mixtures.

Mixtures of equal amounts of 100/600-mesh particles of the two minerals were separated, using terpineol 0.20 lb. per ton and added reagents as shown.

The separation of galena from sphalerite by floating sphalerite away from galena is more difficult than the usual separation in the other direction, but it is possible. This is illustrated by Fig. 57 which records the results obtained on mixtures of pure, slightly oxidized galena and pure sphalerite through the use of xanthate, zinc sulfate, and cyanide, leading to the galena floating first, and those obtained through the use of xanthate, copper sulfate, and potassium chromate, leading to the sphalerite floating first. Although there seems to be little need at present for a method to float sphalerite ahead of galena, the results suggest the possibility of cleaning lead and zinc concentrates by reversing the order of flotation used in roughing.

TABLE 50.—SELECTIVITY INDICES IN LEAD-ZINC-IRON ORES

Source of data	Selectivity indices			
	Lead: zinc	Lead: iron	Lead: all gangue	Lead: non-sulfide gangue
I. Data from Experimental Work				
1. From roughing operations on a complex western ore; data from the laboratory of the author (1926) . . . . .	8 3			
2. From roughing operations on pure deslimed minerals; data from author's laboratory (1927) . . . . .	39.5			
3. From data by C. S. Parsons (quoted in <i>Colorado School of Mines Quarterly</i> ) on complex Canadian ore; roughing only (1927) . . . . .	17.0			
4. From data by C. S. Parsons (same as 3) roughing and cleaning and calculating middling as tailing (1927) . . . . .	13.7			
5. From data published in <i>Colorado School of Mines Quarterly</i> concerning single runs on relatively free-milling mid-western ore (1928), high-lead ore.	28.8			
6. Same as 5, but low-lead ore.	27.1			
II. Mill Data				
7. Collective concentrate from flotation mill treating a jig tailing.			25 6	
8. Selective flotation from complex western ore (1926), Idaho plant.	2 3		19 4	
9. Selective flotation from complex western ore (1926), Idaho plant . . . . .	5 8	15 6		22 4
10. Selective flotation from complex western ore (1925), Montana plant . . . . .	9 6	10 8		77.1
11. Selective flotation from complex western ore (1925), Colorado plant . . . . .	4 0			
12. Selective flotation from complex western ore (1928), Utah plant . . . . .	14 2	15 9		34.8
13. Selective flotation from complex western ore (1929), Montana plant . . . . .	10.9	11.3		73.0*
14. Selective flotation from free-milling ore from the midwestern United States . . . . .	21 5			
15. Selective flotation from free-milling ore from the midwestern United States . . . . .	11 8			
16. Selective flotation from very complex Canadian ore (1929) . . . . .	9 7	19.4		
17. Selective flotation from complex western ore (1928), Utah plant . . . . .	9.0	18.5		53.2
18. Selective flotation from complex western ore (1928), Utah plant. . . . .	6.9	13.1		28.7
19. Selective flotation from complex western ore (1927), Colorado plant. . . . .	6.8			

\* The selectivity index was 176 for the lead-silica separation and 43 for the lead-alumina separation

Generally speaking the selectivity indices obtained in the separation of sulfide lead from sulfide zinc range from 6 to 20 (Table 50), that is, they are much lower than the selectivity indices in the separation of either sulfide from siliceous gangue. All of the data presented in Table 50 are from operations in which cyanide and zinc sulfate or cyanide alone were used except No. 8 which corresponds to the use of zinc sulfate alone, and Nos. 11 and 18, which correspond to the use of sodium sulfite and zinc sulfate.

From the data presented in Table 50 it may be calculated that in 1925-1929 the average (determined geometrically) of the lead-zinc selectivity indices for complex ores was 8.2 whereas that for free-milling ores stood at 21.0: This is largely due to the existence of simpler conditions in the treatment of the free-milling ores, and in particular to the absence of locked particles after grinding. The average lead-iron selectivity index for complex ores was 15.1, or approximately double that obtained for the lead-zinc separation; and the lead-non-sulfide gangue selectivity index was 44. For a given lead recovery in the lead concentrate, and a corresponding zinc recovery, the non-sulfide gangue recovery was about one-thirtieth of the zinc recovery, and the iron recovery one-third of the zinc recovery. Putting it in a different way, it is  $5\frac{1}{2}$  times easier to separate non-sulfide gangue from galena than it is to separate sphalerite from galena; likewise it is three times easier to separate non-sulfide gangue from galena than pyrite and pyrrhotite from galena.

The problem of separating lead sulfide from zinc sulfide has become largely a structural problem, because grinding is not always conducted to insure liberation of the sulfides from each other to the most economical point. Sulfides occur in closer association to each other than to the silicate or other non-sulfide minerals, and require therefore finer grinding than is required to liberate the sulfides from the non-sulfides. Even if perfect liberation is attained and reagents are properly used, it must be kept in mind that it is not possible to separate galena and sphalerite as perfectly as it would be possible to separate galena from an equivalent amount of silicate gangue.

**The Lead-iron Separation.**—The prevention of iron reporting in the lead concentrate is relatively unimportant as iron is needed for lead smelting, and is credited in many lead-smelter

settlements. However, instances are recorded, as in the Flat River District of Missouri, where specific use is made of cyanide to inhibit pyrite and thus raise the grade of the lead concentrate.

**The Zinc-iron Separation.**—The elimination of iron from zinc concentrates is desired for the following reasons:

1. If iron is present in large amount in zinc concentrates, it may result (on roasting the concentrates) in the formation of acid-insoluble zinc oxide-iron oxide compounds ("ferrites") which reduce the amount of zinc extracted by leaching for electrolytic refining.

2. Iron in zinc concentrates increases the bulk of the sludge from the leaching tanks, and thereby dilutes the valuable constituents (largely lead, gold, and silver) contained in that sludge.

3. Zinc concentrates being products of relatively low value, dilution, even with a harmless constituent, is objectionable as it increases the freight-charge burden to be carried by the recoverable zinc in the concentrate.

The separation by flotation of iron sulfides from zinc sulfides is subject to certain limitations which are imposed by the composition of the zinc-bearing mineral. If the zinc mineral is sphalerite, perfect separation from pyrite is theoretically possible but not so if the zinc mineral is marmatite. *Marmatite* is a zinc sulfide in which certain zinc atoms in the crystal lattice are replaced by iron atoms; up to 20 per cent of the zinc atoms in sphalerite may be replaced by iron atoms but the iron content is generally much less than the maximum. The zinc in the Sullivan, B. C., ore body occurs as marmatite containing (1930) approximately 60 per cent Zn and 6.5 per cent Fe. In the older workings of the mine is found a coarsely crystalline marmatite containing 54.5 per cent Zn and 10 per cent Fe<sup>(4)</sup>. The iron content of marmatite is a variable quantity as might well be expected from the fact that it is a solid solution of FeS in ZnS.

Since the iron in marmatite cannot be separated from the zinc by any dressing operation, the existence of marmatite is sometimes asserted without definite proof in order to present metallurgical performances in the best light. In order to determine honestly the limitations of zinc-iron separation on iron-bearing zinc or lead-zinc ores it is necessary to establish definitely the extent to which iron is present in the pure zinc-bearing mineral. This may be done by a combination of hand picking, flotation tests, the microscope, and chemical analysis.

The separation of sphalerite or marmatite from iron sulfides depends upon whether the iron occurs as pyrite or as pyrrhotite. Pyrrhotite is readily oxidized and easier to inhibit than pyrite. This was definitely established in one instance<sup>(12)</sup>: from a 50:50 mixture of pure pyrite and pure pyrrhotite an 80 per cent recovery of pyrite and 80 per cent rejection of pyrrhotite (selectivity index of 4.0) was obtained by flotation with sodium carbonate, 3 lb. per ton, and coal-tar creosote, 0.5 lb. per ton. Little is definitely known about the floatability of marmatite, but it may be expected that it should exhibit the same properties as sphalerite, with a leaning toward the behavior of pyrrhotite.

Marmatitic high-iron zinc ores are frequently characterized by very fine texture and intimate association of the zinc and iron sulfides, so that the operating difficulties and reduced mill performance traceable to mixed particles are superimposed on the other difficulties, and on the requirement for mineralogically purer zinc concentrate set by the lower grade of the pure mineral.

Table 51 summarizes some results obtained in separating pure sphalerite from pure pyrite. Like Fig. 57, Table 52 illustrates the principle that separation of these sulfides can be made through the flotation of one mineral or the other.

TABLE 51.—SEPARATION OF PYRITE FROM SPHALERITE BY FLOTATION\*

Test number	Reagents, lb. per ton						Recoveries, per cent		Selectivity index	
	Terpineol	Ethyl xanthate	Amyl xanthate	Amyl mercaptan	Lime	Copper sulfate	Iron	Zinc	In favor of iron	In favor of zinc
1	0 10	0 02					30	1 2	6 0	
2	0 10	0.05					60	2 1	8 4	
3	0 10	0 10					85	2 6	14 6	
4	0 10	0 15					96	10	14 7	
5	0 10	0 25					99	14	24 6	
6	0 10		0 005				85	1 6	18 7	
7	0.10		0 015				97 5	3 7	32.1	
8	0.10		0 03				99	9 5	30 7	
9	0 10		0 10		2 5	0 10	15	87		6 2
10	0 10		0 10		5 0	0 15	9	89		9.1
11	0 10			0.10	2 5	0 15	4	88		13 1
12	0 10			0 10	5 0	0 15	5	93		15 9

\* Secured in part by C. B. Haynes in the author's laboratory.



Table 52 presents typical selectivity indices for the zinc-iron separation from test work and practice. This table shows that the zinc-iron selectivity index averages 11.1, which is intermediate between the values obtained for the lead-zinc and the lead-iron selectivity indices in the lead cycle (Table 50). It is

TABLE 52.—ZINC-IRON AND ZINC-NON-SULFIDE GANGUE SELECTIVITY INDICES

Source of data	Selectivity indices	
	Zinc: iron	Zinc: non-sulfide gangue
I. Data of an Experimental Nature		
1. Test work on table concentrate which was ground and floated . . . . .	8.2	20.0
2. Test work on jig concentrate which was ground and floated . . . . .	8.9	17.1
3. Dump middling of Canadian mill* (from report by C. S. Parsons) . . . . .	15.6	
II. Data from Mill Operations		
4. Free-milling midwestern ore (1928) . . . . .	....	25.8
5. Montana plant; complex ore (1929) . . . . .	7.6	26.9
6. Montana plant; complex ore (1925) . . . . .	7.5	29.5
7. Idaho plant; complex ore (1925) . . . . .	. .	20.5
8. Utah plant; complex ore (1928) . . . . .	17.7	21.7
9. Utah plant; complex ore (1927) . . . . .	8.8	24.0
10. Utah plant; complex ore (1928) . . . . .	16.0	58.0
11. Canadian plant; complex ore* (1929) . . . . .	14.9†	

\* In these cases the iron occurs as pyrrhotite, in the others as pyrite

† If allowance is made for the fact that the zinc occurs as marmatite, the selectivity index, marmatite: pyrrhotite becomes 33.2.

likely that if the indices were calculated on the basis of the minerals present, rather than on the basis of the metals (that is, if the zinc-iron selectivity indices were not penalized by the iron

held in solid solution in marmatitic sphalerites), the average value of the zinc-iron selectivity index would more nearly approach that of the lead-iron index in the lead cycle than the value of the lead-zinc index in the lead cycle. Putting it differently, the ratio of the floatabilities of sphalerite (or marmatite) to pyrite and pyrrhotite in the zinc cycle would seem to lie somewhere nearer the ratio of the floatability of galena to pyrite and pyrrhotite in the lead cycle than to the ratio of the floatability of galena to sphalerite or marmatite in the lead cycle. From Table 52 it may be inferred that the selectivity index of sphalerite (or marmatite) to pyrrhotite is greater than the index of sphalerite (or marmatite) to pyrite: in other words that pyrrhotite is more readily prevented from floating in the zinc cycle than pyrite. This may be due to the greater ease with which it is oxidized.

After suitable activation sphalerite can be separated from non-sulfide gangue almost as well as galena can be separated from non-sulfide gangue in the lead-floating cycle (Tables 50 and 52). Average selectivity indices are 25 and 44, respectively.

**The Silver and Copper Problem.**—The silver problem arises from the fact that silver is more valuable in a lead concentrate than in a zinc concentrate, and therefore that there is advantage to throwing the silver in the lead product, even at the cost of some of the zinc going in it. From an operative standpoint the problem is made difficult by the fact that the form of the silver is generally unknown. In most sulfide ores in which the occurrence of silver is known, the metal occurs as argentite, a sulfantimonide or sulfarsenide, in solid solution in the galena or in solution in tetrahedrite, tennantite, or chalcopyrite. Generally the silver problem is a structural problem as well as a chemical problem; indeed there are good grounds to believe that the chemical phase of the problem can be solved readily if the structural relations are known. This is because silver minerals must resemble copper minerals in their flotative qualities as well as in their usual chemical properties.

The copper problem is generally a minor one, but as the more important problems are being worked out, more attention is devoted to the recovery of copper. Recovery of copper in the lead concentrate instead of the zinc concentrate is desired as it is of more value there. The greater value of copper in the lead concentrate arises from the fact that copper is an objectionable impurity in zinc concentrates: the zinc-bearing electrolyte,

obtained by leaching the roasted zinc concentrate with sulfuric acid, has to be freed of metals more electropositive than zinc (such as copper) before electrolysis.

The problem of recovering copper in the lead concentrate is structurally and chemically related to that of recovering silver in the lead concentrate.

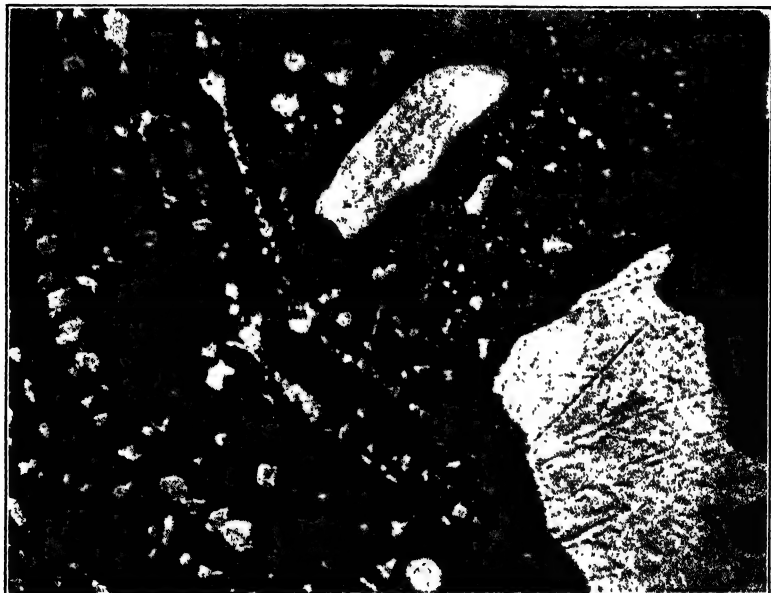


FIG. 58.—Textural relationship of chalcopyrite, galena and sphalerite,  $\times 450$ . The gray groundmass is sphalerite. The two large light-colored blebs are galena. The small light-colored blebs are chalcopyrite. The square in the upper right corner represents the size of an aperture in a 400-mesh screen.

If copper is relatively abundant in a lead-zinc ore it may be economical to segregate it from the lead into a separate copper concentrate (Chap. XI).

The occurrence of minute dots and stringers of copper and silver minerals within sphalerite grains (Fig. 58), and to a lesser degree within galena grains, has been mentioned in Chap. VII (Fig. 21). As the texture of the zinc-silver and zinc-copper associations is frequently much finer than that of the zinc-lead or zinc-iron associations, the grinding that is usually practiced to liberate the lead, zinc, and iron sulfides from each other may be insufficient to liberate the copper and silver minerals occluded in sphalerite (Fig. 58). A relatively smaller recovery of copper

and silver than of lead results in the lead concentrate, together with a larger recovery of silver and copper than of lead in the zinc concentrate. Finer grinding allows a greater proportion of the copper and silver to be recovered with the lead rather than with the zinc.

This is particularly well illustrated by the data presented in Table 53 concerning a lead-zinc ore from Colorado containing substantial quantities of silver and copper. All the tests were made with the same reagents ( $\text{Na}_2\text{CO}_3$ , 3.0 lb. per ton;  $\text{NaCN}$ , 0.25 lb. per ton;  $\text{ZnSO}_4$ , 1.0 lb. per ton, added to the ball mill. K-ethyl xanthate, 0.10 lb. per ton; and cresylic acid, 0.05 lb. per ton, added to the flotation cell).

TABLE 53.—EFFECT OF FINENESS OF GRINDING ON THE RECOVERY OF SILVER AND COPPER IN THE LEAD CONCENTRATE OF A LEAD-ZINC ORE

Test number	Ore ground to			Recoveries in lead concentrate, per cent				Selectivity indices		
	Per cent +100 mesh	Per cent +200 mesh	Per cent +325 mesh	Ag	Cu	Pb	Zn	Ag: Zn	Cu: Zn	Pb: Zn
1	14	32	49	54	21	82	8	3.7	1.7	7.2
2	3	14	26	68	37	86	7	5.3	2.8	9.1
3		1	10	77	55	89	9	5.8	3.5	9.1
4			2	82	71	89	10	6.4	4.7	8.6

Table 53 shows that the lead and zinc recoveries vary but little with increased grinding, so that the lead-zinc selectivity index is practically unchanged; but the silver and copper recoveries increase consistently with fineness of grinding, reflecting more thorough liberation of the minerals. It may be assumed that the copper occluded in the sphalerite reports in the zinc concentrate and that the particles of free sulfide copper report in the lead concentrate. On these assumptions, the difference in the recoveries of copper and zinc, divided by the rejection of the zinc, may be regarded as a measure of the liberation of the copper from the zinc. On that basis, the copper-zinc liberation appears to have been approximately one-seventh, one-third, one-half, and two-thirds complete in the four tests recorded in Table 53.

TABLE 54.—REAGENT CONSUMPTION IN THE TREATMENT OF LEAD ORES  
IN THE UNITED STATES IN 1929

(Treatment of 4,519,154 tons of ore in 34 plants)

(After Muller and Kidd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
<b>I. Frothers</b>				
Pine oils.	23	4,027,344	121,560	0 030
Cresylic acid.	14	4,175,891	430,520	0 103
Total frothers .	20	4,295,825	552,080	0 129
<b>II. Collectors</b>				
1. Distillation Products				
Coal-tar creosotes . .	8	529,752	31,992	0 060
Wood-tar creosotes.	1	2,920,577	2,820	0 001
Pine-tar oils	1	15,694	3,024	0 193
Blast-furnace oils . .	1	25,577	2,513	0 099
Total . .	10	3,475,023	40,379	0 012
2. Synthetic Products				
Xanthates				
Ethyl xanthates	26	1,142,990	270,188	0 236
Amyl xanthates	6	438,986	101,002	0 230
Dithiophosphates (aerofloats)				
Di-cresyl-dithiophosphoric acid .	11	1,384,734	64,538	0 047
Sodium di-cresyl-dithiophosphate	1	2,920,577	102,353	0 035
All other dithiophosphates	1	37,496	33,320	0 880
Thiocarbamid.	2	2,955,154	26,510	0 009
Alpha-naphthylamine	1	37,496	12,380	0 330
Total . .	31	4,518,196	610,291	0 135
Total collectors	34	4,519,154	650,670	0 144
<b>III Acids and Alkalis</b>				
1. Acids				
Sulfuric	1	37,496	272,000	7 254
2 Alkalis				
Sodium carbonate	15	3,808,004	439,811	0 115
Lime	4	3,333,318	2,583,000	0 775
Total alkalis .	17	4,202,245	3,022,814	0 719
<b>IV Other Inorganic Reagents</b>				
1 Sulfidizing				
Sodium sulfide	10	383,795	1,693,142	4 412
2 Activating				
Copper sulfate	5	4,048,798	290,727	0 072
3. Depressing				
Cyanides	7	4,079,838	93,613	0 023
Sodium sulfite.	1	25,577	7,123	0 278
Sodium silicate	5	3,057,722	272,754	0 089
Zinc sulphate	5	3,658,092	250,253	0 068
Total depressing . . . . .	11	4,183,641	623,743	0 149
4 Miscellaneous reagents				
Sodium sulfate . . . . .	1	2,929,577	20,250	0 007
Aluminum sulfate . . . . .	1	2,929,577	15,400	0 005
Total reagents . . . . .	34	4,519,154	7,140,826	1 580

TABLE 55.—REAGENT CONSUMPTION IN THE TREATMENT OF COPPER-LEAD ORES IN THE UNITED STATES IN 1929  
(Treatment of 312,106 tons of ore in nine plants)  
(After Miller and Kidd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
<b>I. Frothers</b>				
Pine oils . . . . .	8	290,502	20,636	0 071
Cresylic acid . . . . .	1	21,604	4,320	0.200
Total frothers . . . . .	9	312,106	24,956	0.080
<b>II. Collectors</b>				
1. Distillation Products				
Coal-tar creosotes . . . . .	2	181,039	16,383	0.090
2. Synthetic Products				
Ethyl xanthates . . . . .	7	201,714	35,369	0 175
Diocetyl-dithiophosphoric acid . . . . .	3	113,474	12,574	0 111
Thiocarbamid . . . . .	2	162,517	15,334	0 094
Total . . . . .	8	249,714	63,277	0 253
Total collectors . . . . .	9	312,106	79,660	0 255
<b>III. Acids and Alkalis</b>				
1. Acids . . . . .				
2. Alkalis				
Sodium carbonate . . . . .	2	162,517	403,114	2 480
Lime . . . . .	5	167,137	283,218	1 695
Total alkalis . . . . .	6	211,007	686,332	3 253
<b>IV. Other Inorganic Reagents</b>				
1. Sulfidizing				
Sodium sulfide . . . . .	2	65,103	83,198	1 278
2. Activating				
Copper sulfate. . . . .	1	118,647	305	0 003
3. Depressing				
Cyanides . . . . .	2	162,517	55,149	0 339
Sodium sulfite . . . . .	1	118,647	1,100	0 009
Zinc sulfate . . . . .	1	118,647	156,181	1 316
Total depressing . . . . .	2	162,517	212,430	1 307
Total reagents . . . . .	9	312,106	1,086,881	3.482

TABLE 56.—REAGENT CONSUMPTION IN THE TREATMENT OF ZINC ORES  
IN THE UNITED STATES IN 1929  
(Treatment of 2,529,253 tons of ore in 109 plants)  
(After Miller and Kidd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
<b>I. Frothers</b>				
Pine oils	90	2,320,273	282,532	0.122
Cresylic acid	63	1,190,238	100,090	0.084
Total frothers.	109	2,529,253	382,622	0.151
<b>II. Collectors</b>				
1. Distillation Products				
Coal-tar creosotes	52	1,504,517	182,123	0.121
Wood-tar creosotes	2	164,068	22,486	0.137
Petroleum products	2	186,094	627	0.003
Blast-furnace oils	1	209,603	20,960	0.100
Linseed oil	2	44,000	420	0.010
Total.	57	1,967,566	226,616	0.115
2. Synthetic Products				
Xanthates:				
Ethyl xanthates	89	1,766,582	314,875	0.178
Amyl xanthates	2	518,461	4,454	0.009
Dithiophosphates:				
Dicresyl-dithiophosphoric acid	29	580,556	62,614	0.108
Sodium dicresyl-dithiophosphate	14	466,636	24,307	0.052
Thiocarbamid.	1	323,011	33,900	0.105
Alpha-naphthylamine	11	189,000	11,091	0.059
Total	108	2,509,253	451,241	0.180
Total collectors	109	2,529,253	677,437	0.268
<b>III. Acids and Alkalis</b>				
1. Acids				
Sulfuric	1	19,348	11,095	0.573
2. Alkalis				
Sodium carbonate	5	94,348	23,337	0.247
Sodium hydroxide	1	12,612	415	0.033
Lime	25	879,142	2,540,218	2.889
Total alkalis	30	966,754	2,563,970	2.652
<b>IV. Other Inorganic Reagents</b>				
1. Sulfidizing				
Sodium sulfide	1	20,000	616	0.031
2. Activating				
Copper sulfate	109	2,529,253	2,554,580	1.010
3. Depressing				
Cyanides	8	214,500	9,712	0.045
Sodium sulfite	1	19,348	235	0.012
Sodium silicate	13	163,228	15,363	0.094
Total depressing	21	377,728	25,310	0.067
Total reagents	109	2,529,253	6,216,050	2.458

TABLE 57.—REAGENT CONSUMPTION IN THE TREATMENT OF LEAD-ZINC ORES INCLUDING TWO PLANTS TREATING LEAD-ZINC-IRON ORES IN THE UNITED STATES IN 1929  
(Treatment of 3,693,243 tons of ore in 43 plants)  
(After Muller and Kudd.)

Reagents	Plants using	Tons ore treated	Reagent consumption, lb.	
			Total	Per ton
<b>I. Frothers</b>				
Pine oils . .	33	3,106,494	269,302	0.087
Cresylic acid .	28	2,562,550	303,209	0.118
Orthotoluidin.	3	248,593	27,585	0.111
Total frothers	42	3,371,755	600,096	0.178
<b>II. Collectors</b>				
1. Distillation Products				
Coal-tar creosotes	21	1,729,919	514,564	0.297
Coal tars . . .	2	362,057	25,945	0.071
Wood-tar creosotes	5	1,106,237	92,663	0.084
Blast-furnace oils	2	365,580	44,311	0.121
Total.	24	2,149,564	677,483	0.315
2. Synthetic Products				
Xanthates.				
Ethyl xanthates	38	3,258,617	676,803	0.208
Amyl xanthates	1	308,892	4,942	0.016
Dithiophosphates				
Dicresyl-dithiophosphoric acid	17	2,220,087	185,679	0.084
Sodium dicresyl-dithiophosphate.	3	485,745	51,914	0.107
Thiocarbamid.	7	1,020,436	76,875	0.075
Total	40	3,559,074	996,213	0.280
Total collectors.	43	3,693,243	1,673,696	0.453
<b>III. Acids and Alkalis</b>				
1. Acids . . . . .	.....	.....	.....	.....
2. Alkalis				
Sodium carbonate	28	2,525,194	2,882,848	1.142
Sodium hydroxide	1	86,800	7,923	0.091
Lime . . . . .	22	1,964,577	4,08,562	2.397
Total alkalis.	38	3,222,992	7,599,333	2.358
<b>IV. Other Inorganic Reagents</b>				
1. Sulfidizing				
Sodium sulfide.. .	3	628,498	258,804	0.412
2. Activating				
Copper sulfate . . .	42	3,665,475	3,625,575	0.989
3. Depressing				
Cyanides. . . . .	26	2,048,609	591,750	0.289
Sodium sulfite. . .	6	830,146	805,287	0.970
Sodium silicate. . .	2	343,022	23,667	0.069
Zinc sulfate . . .	35	3,221,948	2,454,341	0.762
Total depressing. . .	39	3,398,375	3,875,045	1.140
4. Miscellaneous				
Calcium chloride.....	1	159,814	92,092	0.580
Sodium chloride.....	2	78,368	103,124	1.316
Total reagents . . . . .	43	3,693,243	17,828,455	4.827



Table 53 shows that the silver is not so closely associated with sphalerite as is the copper.

Microscopic examination supported the flotation data, showing chalcopyrite and tetrahedrite inclusions in sphalerite, some of them possibly silver bearing, and tetrahedrite inclusions in galena.

#### REAGENT CONSUMPTION

The flotation of straight-lead and of straight-zinc ores is simple. Reagent consumption and expenditure are therefore low (Tables 54, 55, and 56<sup>(15)</sup>). In 1928 average reagent cost per ton was about 6 cts. for straight-lead ores, 13 cts. for lead ores containing a substantial amount of copper, and 13 cts. for straight-zinc ores.

The flotation of lead-zinc ores and of lead-zinc-iron ores, on the other hand, required a greater quantity of reagents (Table 57<sup>(15)</sup>). In 1928 average reagent cost for these ores was 23 cts. for lead-zinc ores and 29 cts. for lead-zinc-iron ores.

#### PRACTICE

The great variety in lead and zinc ores makes it desirable to review the practice at a number of concentrators. The following examples have been selected as typical of the various ores: (a) a Missouri lead plant; (b) the Kansoria plant of the Federal Mining and Smelting Company, in the Tri-state District; (c) the Morning plant of the Federal Mining and Smelting Company at Mullan, Idaho; (d) the Timber Butte mill of the Anaconda Copper Mining Company at Butte, Mont.; (e) the Sullivan mill of the Consolidated Mining and Smelting Company at Kimberley, B. C.; (f) the Tooele mill of the International Smelting Company at Tooele, Utah; (g) the Midvale mill of the United States Smelting, Mining and Refining Company at Midvale, Utah.

The Missouri lead plant treats by all-flotation a galena lead ore in which the gangue is a crystalline dolomitic limestone, in which there is practically no sphalerite and but small quantities of pyrite. The Kansoria plant treats by flotation the fine portion of a straight-sphalerite zinc ore. The Morning mill treats an ore in which the lead-zinc ratio is high and in which there is little sulfide iron. The ore treated at Timber Butte is typical of ores in which the lead-zinc ratio and iron-zinc ratio

are low. The ore treated at the Sullivan mill is typically high in iron, the zinc occurring as marmatite and the iron largely as pyrrhotite. The Tooele mill is a custom mill treating various types of ores in which the lead, zinc, and iron contents are of the same order of magnitude. The Tooele mill makes three concentrates, that is a pyrite concentrate in addition to the lead and zinc concentrates. The Midvale mill also makes three con-

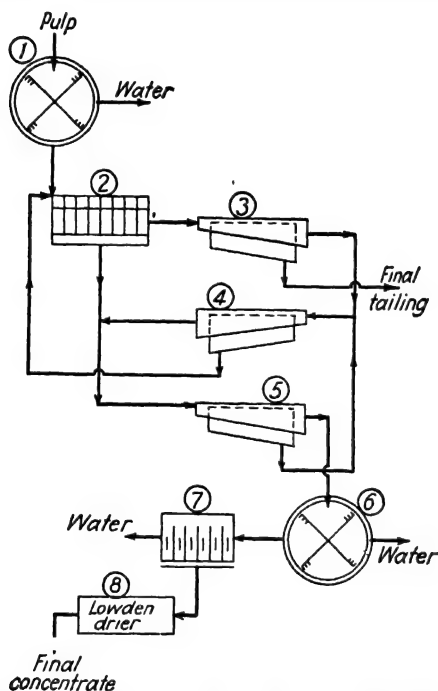


FIG. 59.—Flotation division, Missouri lead plant.

centrates from custom ores. It has been included in this selection because of the great difference in the reagents employed there as compared to those employed at Tooele.

**Missouri Lead Plant.**—The Missouri lead plant described here has recently been remodeled, flotation replacing gravity concentration and resulting in increased recovery of the lead, increased grade of the concentrate, and a much simplified flow-sheet (Fig. 59).

After grinding and thickening, (1), the pulp is floated in Fahrenwald sub-aeration cells (2), followed by a pneumatic scavenger (3), whose tailing is a finished product containing lead to the extent

of 0.05 to 0.10 per cent; the concentrate from the scavenger cell is cleaned once in a pneumatic scavenger cleaner (4), and the cleaner tailing is returned at the head of the rougher. The scavenger-cleaner concentrate and the rougher concentrate are cleaned further in a recleaner (5) of the pneumatic type. The tailing from the recleaner is returned at the head of (4) and the concentrate is thickened (6), filtered (7), and dried further in a Lowden drier (8) to a moisture content of 7 per cent.

The ore treated is characterized by its simplicity, as it is composed of coarse galena with small amounts of pyrite in a dolomitic gangue. The gangue compels the flotation circuit to be alkaline; this in itself is a helpful circumstance. The absence of clayey, flaky alteration minerals makes it possible to effect excellent gangue rejection without material loss of galena. The feed contains lead to the extent of about 5 per cent; the concentrate, 80 per cent; and the tailing, 0.05 to 0.10 per cent; indicating a lead recovery of 97 to 99 per cent. The galena: gangue selectivity index ranges from 120 to 200, a very high value, indeed.

The reagents used are aerofloat, 0.08 lb. per ton, and cresylic acid, 0.08 lb. per ton.

**The Kansoria Plant**<sup>(28)</sup>.—This plant is typical of many plants in the Tri-state District in which flotation is used as an adjunct to gravity concentration. The fine particles formed during grinding, and the reground table and jig tailings, are treated for the recovery of the zinc in a rougher-scavenger circuit in which the rougher makes a final concentrate and the scavenger a middling returned at the head of the rougher. The small amount of lead in the ore is collected in this concentrate and separated from the zinc by tabling the finished concentrate. Metallurgical results are satisfactory, particularly in consideration of the very simple treatment: the feed contains approximately 12 per cent zinc, giving a concentrate containing about 57 per cent zinc and one per cent lead, and a zinc recovery in the vicinity of 95 per cent. The selectivity index between sphalerite and non-sulfide gangue is in the vicinity of 30.

The reagents used are potassium xanthate, 0.57 lb. per ton; copper sulfate, 2.0 lb. per ton; pine oil, 0.13 lb. per ton; Barrett No. 634 oil, 0.08 lb. per ton.

**The Morning Mill.**—The minerals in the ore from the Morning mine are galena, sphalerite, a very small quantity of pyrite,

chalcopyrite, siderite, miscellaneous carbonates, such as calcite and dolomite and siliceous material (quartzite). From the point of view of flotation the gangue is a relatively simple one to deal with as there are no minerals that form flaky particles to pollute the concentrates (as in the case of ores having a gangue of decomposed granite). However, the minerals are extremely intimately associated, and intergrowths of galena and sphalerite requiring fine grinding to unlock are common. A. W. Fahrenwald<sup>(7)</sup> has pointed out the structural difficulties of the Coeur



FIG. 60.—Complex galena-sphalerite particle, Morning mill,  $\times 350$ .

Particle occurred in the 100/150-mesh size of the zinc concentrate. The light areas are galena; the dark areas, sphalerite. The dark gray groundmass is bakelite. The square in the upper left corner indicates the size of an aperture in a 400-mesh screen.

d'Alene ores. Figure 60 shows a mixed particle from the present (1930) zinc concentrate. The association of the minerals is so extreme in this particle that grinding to 3000 mesh (5 microns) would probably be inadequate to effect complete liberation. Fortunately associations such as shown by Fig. 60 are not typical, or else selective flotation would be impracticable.

The present flow-sheet (Fig. 61) of the Morning mill embodies a regrinding circuit applied to the middling made in the lead circuit and another applied to the middling made in the zinc circuit<sup>(26)</sup>.

The lead middling is obtained as a concentrate from the last six cells of a battery of Owen and Dalton (O. & D.) sub-aeration

roughing cells and is relatively low in lead content and high in zinc content. Examination under the microscope of this middling product shows that a large portion of the particles are true

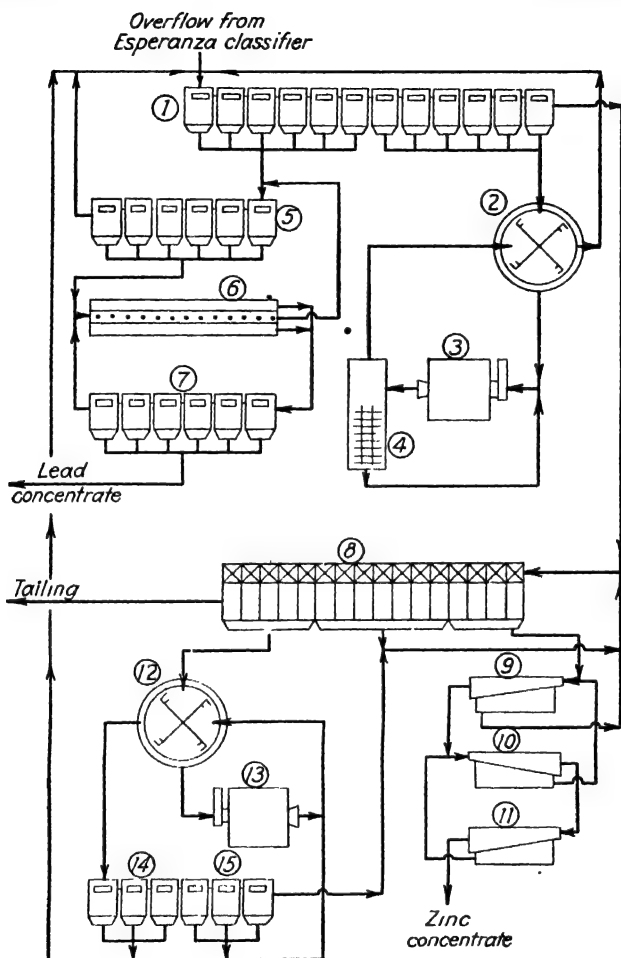


FIG. 61.—Flotation and regrinding division, Morning mill.

middling particles. These particles have been floated because of having some galena at the surface.

The zinc middling is obtained as a concentrate from the last five cells of four batteries of 16 M.S. cells in series. It is relatively low in zinc but contains more lead than might casually be expected. Most of the particles have some sphalerite at

their surface which explains their flotation as a zinc middling. The older flow-sheet<sup>(3)</sup> did not have these regrinding circuits; as a result the metallurgical results were not as good as those currently obtained. For instance, introduction of the zinc regrinding circuit and minor reagent changes have permitted a raise of the grade of the zinc concentrate from 51 to 57 per cent at no sacrifice in recovery.

The flow-sheet is as follows (1930). The classifier overflow goes to O. & D. flotation machines ① which make a rougher lead concentrate from the first six cells and a lead-zinc middling (locked particles) from the next six cells. The middling goes first to a small Dorr thickener functioning as a classifier ②; the overflow from the thickener returns at the head of the lead cells. The product that is so returned consists of particles that are presumably too fine to be middling particles. The underflow from ② goes to a ball mill ③ in closed circuit with a classifier of the rake type ④; the classifier overflow returns to the thickener classifier ②, and then to the head of the lead floating cycle. Thus, the regrinding of the middling features two classifiers in series—a rather unusual procedure, but one that might well be adopted for effectiveness in classifying. The rougher concentrate from ① goes to a six-cell O. & D. cleaner ⑤, the concentrate from ⑤ to a Forrester recleaner ⑥, and the concentrate from ⑥ to a six-cell O. & D. re-recleaner ⑦. The tailing from each machine in these cleaning steps is returned at the head of the preceding machine. The tailing from ① is the deleaded pulp ready for zinc flotation.

For zinc flotation the tailing from ① goes to four batteries of two eight-cell M.S. machines in series ⑧. The first four cells in each battery make a rougher concentrate which is cleaned, recleaned, and re-recleaned, countercurrent fashion in 10-ft. Callow cells ⑨, ⑩, ⑪. There are six cleaners, five recleaners, and four re-recleaners. Cells 5 to 11 inclusive in the rougher ⑧ make a middling which is returned at the head of the first cells, and the last five cells of the rougher make a middling to be reground and a final tailing which goes to waste. The middling to be reground is classified in an 18-ft. classifying Dorr thickener ⑫, the underflow of which is ground in an 8-in. by 22-ft. Harding mill in closed circuit ⑬. The reground middling is floated for lead in a three-cell O. & D. machine ⑭, the leady product being returned at the head of the main lead circuit. The tailing from

⑭ is floated further in another three-cell O. & D. machine ⑮ which makes a middling returned to the classifying thickener and a tailing which is returned to the head of the main zinc circuit.

The reagents used are as follows. For lead flotation: zinc sulfate, 0.26 lb. per ton; aerofloat (dithiophosphoric acid), 0.11 lb. per ton; cresylic acid, 0.03 lb. per ton. For zinc flotation: copper sulfate, 0.47 lb. per ton; sodium xanthate, 0.25 lb. per ton; Barrett No. 4, 0.22 lb. per ton. Lime to the extent of 1.4 lb. per ton of concentrate is used to promote the flocculation of the concentrate in the thickeners. Pine oil to the extent of 0.3 lb. per ton of lead concentrate is added to make a drier filter cake: it reduces the moisture content of the filter cake by 2 per cent. The total cost of reagents varies between 10 and 13 cts. per ton, depending upon the exact amounts used and the price of the commodities. Of this cost about six-tenths is for zinc flotation.

Metallurgical results are presented in Table 44. The improvement from year to year is apparent. The recent increase in the grade of the lead concentrate has been brought about by the introduction of an additional cleaning step. The galena: non-sulfide-gangue selectivity index now is in the vicinity of 70, whereas three years ago it was in the vicinity of 30.

**The Timber Butte Mill.**—The Timber Butte mill of the Anaconda Copper Mining Company, located at Butte, Mont., has been treating daily about 1300 tons of the lead-zinc ores of the Butte District together with some custom ores from neighboring districts in Montana and Idaho. The ores from the Butte District were long regarded as zinc ores, and as such were concentrated by flotation as far back as 1912. For the past 8 years, however, it has been found increasingly possible to segregate the lead from the zinc, although the lead occurs in small bulk compared to the zinc. The low lead-zinc ratio has made it difficult to secure both a high-grade lead product and a high lead recovery in the lead concentrate, and has led to the development of a rather unusual type of flow-sheet.

Besides galena and sphalerite, the ore contains some pyrite, also silver and copper in various forms. The gangue is largely a decomposed granite containing feldspars, quartz, and secondary silicate minerals such as sericite. The silver and copper occur in various forms, as coarsely dispersed silver-bearing copper

minerals such as enargite, in fine-textured association with the lead mineral, and occluded in the sphalerite.

The Timber Butte ores frequently contain large quantities of soluble salts, particularly those composed of the following ions: sulfate, calcium, magnesium, carbonate, ferric, and zinc. Some of these salts have a favorable selective action, for instance the zinc salt which assists in the separation of galena from sphalerite; others are objectionable and must be diluted by mixing the ore with ores containing small amounts of soluble salts. Generally, if an ore has over 8 to 10 lb. of soluble salts per ton it must be diluted before satisfactory flotation results. The ores having a kaolinized gangue are difficult to handle in all the dressing steps: in the crushing and grinding stages where the fine silicate minerals pack and reduce the capacity of the crushing machines; in the classifiers which are taxed because of the imperfect dispersion of the fine particles; and in flotation where adherence of fine silicates to sulfides makes the sulfides difficultly floatable, and where mechanical overflow of the fine sericite and kaolin particles with the interbubble water reduces the grade of the concentrate.

The flow-sheet is shown in Fig. 62. The classifier overflow goes to a surge tank ① where the composition of the pulp is equalized and contact time with reagents is obtained, thence to one 20-cell M.S. flotation machine ② from which a rougher lead concentrate is drawn from the first 15 cells and a lead middling from the last five cells. The middling is returned to surge tank ① and the rougher concentrate is cleaned in one Callow cell ③ whose tailing is also returned to the surge tank. The concentrate from ③ is a low-grade lead product containing much zinc and has to be treated further to be suitable for lead smelting. Zinc-inhibiting reagents are added to this primary lead concentrate at this point, and the proper time of contact, with heat, is allowed in conditioning tank ④. From this tank the pulp proceeds to three Callow flotation machines in which the lead, copper, and silver are floated but the zinc is inhibited. These three Callow cells are arranged as a roughing, cleaning, and recleaning cycle, the tailings from the first two, ⑤ and ⑥, being generally returned to the primary-lead cleaner ③, and the tailing from ⑦ being returned to the head of ⑤. It might be noted at this point that the Timber Butte flow-sheet is very flexible—a desirable feature in a mill treating a variety of ores. Flexibility



in the flow-sheet is particularly well shown in the lead retreatment cycle, the tailing from ⑦ being capable of returning to ⑥, to ③, or to ⑤, and the tailing from ⑧ being routed to ⑤ or to ③, as desired. The concentrate from ⑦ is the finished lead

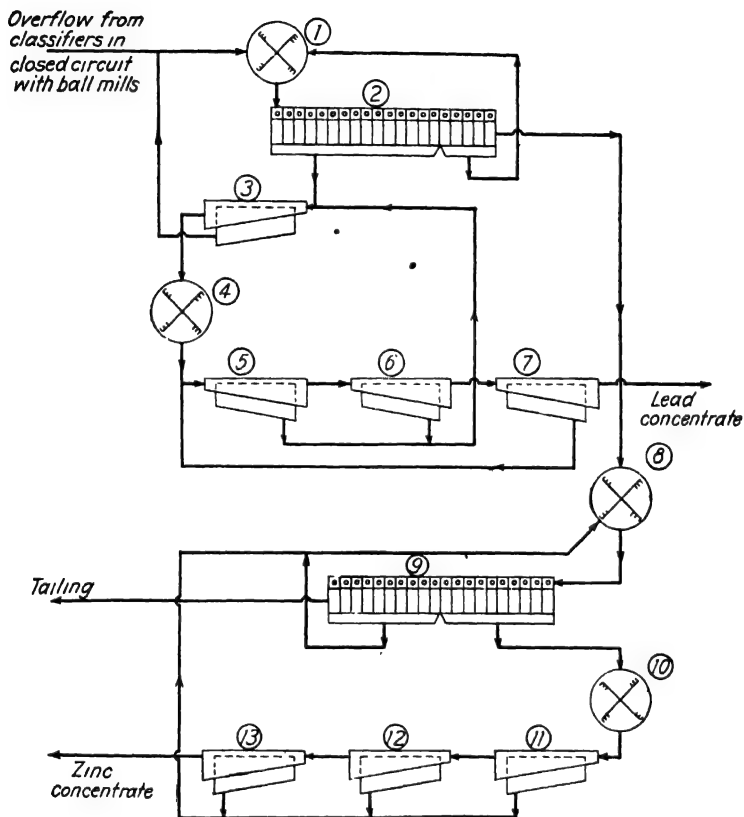


FIG. 62.—Flotation division, Timber Butte mill.

concentrate. The tailing from ② is the deleaded pulp which is ready for zinc flotation.

For zinc flotation the tailing from ② is first conditioned with the zinc-floating reagents in tank ⑧ and then floated in three standard M. S. flotation machines ⑨ consisting of 20 cells of which the first 10 produce a rougher zinc concentrate and the last 10 a middling returning to the head of the machine. The rougher zinc concentrate goes to a surge tank ⑩, then it is cleaned in

three steps in Callow cells ⑪, ⑫, ⑬ similar to the three steps by which the lead product is cleaned.

The feature of the Timber Butte flow-sheet lies in that no attempt is made to prevent the zinc from floating to some extent in the primary lead circuit; rather some of the zinc is allowed to float with the lead in order to collect at the same time a greater proportion of the lead and copper in the primary lead float. This scheme has the advantage of reducing the consumption of zinc-inhibiting reagents. This reduction results from the application of these reagents to a relatively small portion of the total sphalerite in the ore, and from their application to a primary concentrate of small bulk rather than to the total pulp. The special flow-sheet employed at the Timber Butte plant permits the use of heat in the retreatment of the primary concentrate—an operation which might be too expensive if performed on the total pulp.

Pulp heating in the retreatment section increases the effectiveness of the zinc-inhibiting reagents and, at the same time, increases the lead recovery that results after this conditioning. The increase in effectiveness of the zinc-inhibiting reagents brings about a decreased reagent consumption. Other advantages of heating the pulp may result from the corresponding decrease in pulp viscosity and from an increased speed of reaction

TABLE 58.—FLOTATION REAGENTS IN USE AT TIMBER BUTTE MILL, 1929  
(After Morrow.)

Reagent	Quantity added, lb. per ton ore	Place of addition
Cleveland Cliffs No. 1 hardwood creosote oil..	0 12	Crushing rolls
Lime .....	1 7	Classifiers in closed circuit with ball mills
Xanthate (K-ethyl) . .	0 2	Lead middling from ①
Calcium cyanide. . . .	0.6	Lead retreatment condition- ing tank ④
Zinc sulfate .....	0 6	Lead retreatment condition- ing tank ④
Copper sulfate .. . . .	1 8	Zinc conditioning tank ⑧
Lime.....	1 3	Zinc conditioning tank ⑧
Barrett No. 4.....	0 14	Zinc conditioning tank ⑧
Pine oil.....	0 015	Zinc conditioning tank ⑧

between dissolved chemicals and the surfaces of the minerals. In the retreatment tanks the pulp is heated to about 140°F.

The reagents used and place of addition are presented in Table 58. Besides these reagents there is added for some ores a substantial amount of calcium chloride.

Metallurgical results have been improved consistently since the plant adopted selective flotation. Table 59 presents some recent results (first half of 1929). In considering the results obtained it might be mentioned that some 50 or 60 different ores were treated during this period by the Timber Butte mill, coming from various parts in Montana and Idaho. The two cases selected and presented in Table 59 represent extremes of practice, the aim in case *A* being to recover as much of the copper in the lead concentrate as possible, and in case *B* to make a high-grade lead product in which as small a zinc recovery as possible

TABLE 59.—METALLURGICAL RESULTS AT TIMBER BUTTE MILL  
(After Quigley (19).)

Metallurgical Data	Case A*			Case B†		
	Feed	Lead concentrate	Zinc concentrate	Feed	Lead concentrate	Zinc concentrate
Grade						
Au, oz per ton	0 015	0 122	0 024	0 020	0 172	0 029
Ag, oz per ton	6 55	116 9	13 5	6 98	120 5	17 0
Cu, per cent.	0 38	7.05	0.73	0 26	3 2	0.70
Pb, per cent	1 90	45.8	1.73	2 44	64.5	2.49
Zn, per cent	11 0	13.9	58.1	11 6	8.1	57.2
Fe, per cent	3.7	4.9	2.9	4 5	2.6	2.5
Insol, per cent	66 6	3.4	3 3	62 5	1 3	4 3
Selectivity Indices in Lead Circuit						
Lead-zinc		8 0			10 0	
Copper-zinc		5 7			5 0	
Silver-zinc		5 4			6 3	
Lead-insoluble		40 4			58 0	
Lead-iron		7 7			8 1	
Selectivity Indices in Zinc Circuit						
Zinc-insoluble			57 5			37 2
Zinc-iron			13 5			12 6

\* Making a high copper recovery in the lead concentrate.

† Making a high-grade-lead, low-grade-zinc, lead concentrate.

is made. The effect of these alternative practices on the various selectivity indices should be noted.

**The Sullivan Plant<sup>(5)(17)</sup>.**—The Sullivan plant of the Consolidated Mining and Smelting Company of Canada, Ltd., is located near Kimberley, B.C., Canada, and treats the ore from the famous Sullivan mine. This ore (Fig. 63) is composed of galena, marmatite, pyrite, and pyrrhotite, with little silicate gangue. The sulfides occur in an extremely fine state of division, resembling a matte. The fine state of division of the sulfides and the large quantity of iron in relation to lead and zinc have constituted a serious obstacle to the treatment of the ore. It is not until after many trials, but with the determination to



FIG. 63.—Sullivan ore,  $\times 800$ .

Camera-lucida drawing of matte-like intergrowth of galena (white), marmatite (black), and pyrrhotite (stippled).

overcome the difficulties, that the staff of the Company has succeeded in devising a treatment method. For about 8 years the ore has been treated by selective flotation, constant improvements resulting in today's splendid metallurgical performance. Daily plant capacity is now about 6000 tons.

As compared with the ores whose treatment has been described in the foregoing pages, the Sullivan ore is characterized by the much higher iron sulfide content. The ratios by volume of iron sulfides to galena and of iron sulfides to marmatite are about 100:10 and 100:20. For comparison it may be noted that the ratios by volume of the iron sulfides to galena and to sphalerite are respectively 100:25 and 100:350 in the Butte

ores, and 100:20 and 100:90 in the ores of the Salt Lake region. It may therefore be considered that the iron-rejection problem is about twice as acute in the lead circuit and four to fifteen times more acute in the zinc circuit of the Sullivan mill than in that of concentrators treating other complex lead-zinc-iron ores. It is no doubt a fortunate circumstance that most of the iron in the Sullivan ore occurs as pyrrhotite, rather than as pyrite, as pyrite is materially more difficult to inhibit than pyrrhotite.

Fine grinding is required on account of the very fine dissemination of the sulfides in each other. The grinding involves considerable expenditure of energy because of the very solid, massive, character of the ore. To limit the fine-grinding expenditure a rather complex flow-sheet has been evolved which comprises several fine-grinding steps and the regrinding of middlings after roughing flotation operations have been concluded. Figure 27 (Chap. VII) shows the grinding section of the flow-sheet (as of the summer of 1930) and Fig. 64 the flotation section of the same.

The overflow from the classifier ② (Fig. 64) in closed circuit with the tertiary ball mills ③ goes to a conditioning tank ④, then to a pulp distributor ⑤ which feeds six 18-cell M.S. roughers ⑥. A rougher lead concentrate is removed from the first 15 cells and a middling from the last three. The middling is returned to the head of the secondary classifier ① which overflows into the tertiary classifier ②. The rougher lead concentrate is cleaned twice in eight-cell M.S. flotation machines ⑦ and ⑧; the cleaner tailing goes to the secondary classifier ① and the recleaner tailing goes to the head of the cleaner. The recleaner concentrate is the finished lead concentrate.

The tailing from ⑥ is treated for recovery of the zinc content as follows: the pulp is first conditioned in surge tank ⑨, then fed to four 18-cell M.S. zinc roughers ⑪, by the four-way pulp distributor ⑩. The first 12 cells of the zinc rougher make a rougher zinc concentrate and the last six a middling. The rougher zinc concentrate is cleaned twice, the flow being similar to that for the cleaning of the lead concentrate; the only difference is that the rougher zinc middling and the cleaner zinc tailing, instead of returning to the secondary classifier ①, go to a separate regrinding circuit composed of two classifiers ⑭, and one ball mill ⑮. The retreatment classifier overflows to a thickener ⑯ thence to a conditioning tank ⑰ before retreatment flotation



tion. Upon adjustment of flotative conditions to secure a lead concentrate, the particles of pure galena float first; then come middling particles of galena and marmatite, and of galena and pyrrhotite in which galena is the dominant surface constituent; and later come middling particles in which the proportion of the total surface occupied by galena is less than in the first middling particles to float. Thus, by collecting a middling product as well as a rougher concentrate from the rougher lead cells ⑥, a crude segregation of the middling particles is made. This effect is accentuated in the cleaner machine. The middling product returned for regrinding consists largely of middling particles composed of galena and marmatite and of galena and pyrrhotite, together with some particles of pure pyrrhotite or of pure marmatite. In the zinc circuit, the remaining middling lead-zinc particles are floated, but not ahead of the pure marmatite grains. This is because of the addition of certain lead-inhibiting reagents (see below). The middling particles recovered in the zinc-floating cycle are collected with the marmatite-pyrrhotite middling particles in the last cells of the zinc rougher or are rejected in the zinc-cleaner tailing. The combined zinc-cleaner tailing and rougher middling is similar to the combined lead-cleaner tailing and lead-rougher middling except in two respects: it contains relatively more zinc and less lead, and it has been acted upon by reagents that are designed to inhibit galena and pyrrhotite rather than by reagents designed to inhibit marmatite and pyrrhotite. On this account the zinc-rougher middling and the zinc-cleaner tailing are not returned to the secondary classifiers for further grinding; they are reground, conditioned, and floated in a separate circuit.

The reagents used include soda ash, sodium cyanide, sodium dichromate, copper sulfate, cresylic acid, water-gas tar, and coal-tar creosote. These reagents differ in several respects from those used in other lead-zinc plants. The first difference worthy of note is the absence of chemical collectors, such as xanthates. Extensive experiments have been made with them, but they have not proved as effective as oils; the objection to their use arises from the fact that they float more pyrrhotite and pyrite, particularly in the lead concentrate. The second point worthy of note is concerned with the use of sodium dichromate. This reagent is added as a galena and pyrrhotite depressant in the zinc circuit; it has resulted in a considerable improvement in the grade

of the zinc concentrate, exerted a steadying influence on the lead grade and recovery, and effected a small increase in zinc recovery. The third point of interest is in connection with the place of addition of the reagents, and the extensive use of conditioning tanks to allow for reaction between reagents and minerals. The cyanide used is added in part at the head of the lead circuit to inhibit zinc and iron minerals, and in part to the zinc-middling regrinding and thickening circuit to deactivate the previously activated sphalerite.

TABLE 60.—REAGENTS USED AT SULLIVAN MILL, 1929

Reagent	Approximate amount, lb. per ton	Place of addition
Soda ash. . . . .	4 0	Ball mills.
Copper sulfate.	1 0	Conditioning tank ⑨.
Sodium cyanide.	0 10	Ball mills.
Sodium cyanide	0 10	Zinc middling regrinding circuit.
Oil mixture*.	0 30	Lead circuit.
Oil mixture*.	0 15	Zinc circuit.
Cresylic acid.	0 10	Lead circuit.
Sodium dichromate.	0 1	Zinc circuit.

\* A mixture of coal-tar creosote and water-gas tar.

TABLE 61.—TYPICAL METALLURGICAL RESULTS AT SULLIVAN MILL

Product	Assay				
	Ag, oz. per ton	Pb, per cent	Zn, per cent	Fe, per cent	Insoluble, per cent
Feed. . . . .	4 0	8 5	7.5	36.0	12.0
Lead concentrate	24 0	69 5	5 0	6 0	1 2
Zinc concentrate	2 0	3.3	50 0	11 6	1.4

NOTE.—Metallurgical efficiency(®), 89 per cent.

Table 60 gives the reagents used and the place of addition. Table 61 summarizes typical metallurgical results.

**The Midvale Plant**<sup>(11)(14)</sup>.—The Midvale plant of the United States Smelting, Refining and Mining Company is located at Midvale, Utah, and treats ores from the Bingham and Park City districts of Utah. Like the Timber Butte mill, this is a custom



plant treating ores from many shippers although the bulk of the ore comes from one or two mines. On account of the variations in the ores, the plant has been arranged in three sections, so that each can treat a different ore or mixture of ores as desired. In general the ores from Bingham are treated alone in one or two sections of the mill, and the remainder is treated in the other section. Considerable attention is given to proper mixing of ores to get a feed of relatively uniform character, composition, soluble salts, structure, and texture. To this effect the plant has been equipped with an extensive bin system from which feeding can proceed as slowly or as rapidly as desired. Capacity is about 800 tons daily.

This mill is making three concentrates: a lead concentrate, a zinc concentrate, and an iron concentrate. It differs therefore from the mills studied so far in that an iron concentrate is made. It may be of interest to note that an iron concentrate could be produced at many plants if economic conditions warranted<sup>(2)</sup>.

What has made desirable the production of an iron concentrate in the Salt Lake Valley has been the existence of extensive oxidized siliceous lead-silver ores in the Tintic District which until recently could not be concentrated at a profit. Iron is necessary to flux silica in the lead blast furnaces, so that a premium for iron has been the rule in the Salt Lake Valley. This has led to the production of iron concentrates by flotation. Even this situation would not justify the production of iron concentrates and the additional operation would not have been undertaken, had it not been for the fact that the pyrite concentrates made from the lead-zinc-iron ores of the Salt Lake Valley contain appreciable quantities of lead, silver, and gold.

The following illustrates the economics of the problem. If the premium for iron is 6 cts. per unit, an iron concentrate containing 40 per cent iron is worth to a lead smelter at least \$2.40 for its iron content; against this must be charged the silica content of the iron concentrate and the treatment charge for roasting and smelting the material. Even on a 40 per cent iron concentrate, these charges would exceed \$2.40 considerably; it is clear therefore that an iron concentrate has to contain some valuable metals besides iron in order to have any real value to a lead smelter. As a matter of fact the iron concentrates made in the Salt Lake Valley for lead-smelting purposes contain a substantial amount of gold and lead not previously recovered in the

lead and zinc circuits. The value of the iron concentrate is so small that should conditions change sufficiently for the premium on iron to disappear or even shrink to 2 or 3 cts. per unit, the cost of making a gold- and lead-bearing iron concentrate might well begin to exceed its value. Such an event is not at all unlikely with the concentration by flotation of the siliceous ores of the Tintic District which is now being undertaken on a large scale. The next few years may therefore see the Midvale and the Tooele plants reduce materially their production of iron concentrate in proportion to their production of lead and of zinc concentrates.

The ore milled at Midvale is higher in pyrite than that milled at Timber Butte, but it contains less iron than the Sullivan ore. Also, the amounts of lead and zinc in the ore are about the same, which is not the case with the Timber Butte mill, but is the case for the Sullivan, Morning, and Tooele mills. The principal minerals in the ores milled at Midvale are galena, sphalerite, and pyrite. The minerals are more coarsely aggregated than in the Idaho and Sullivan ores; this is particularly true of the ores from the Park City District.

The flotation division of the flow-sheet is shown in Fig. 65. From the classifiers in closed circuit with ball mills, the pulp overflows to a Devereux agitator ① which acts as a surge tank, thence to the lead flotation rougher ② which is a 12-cell sub-aeration machine; a finished lead concentrate is drawn from the first four cells and a middling is drawn from the last eight. The middling is returned at the head of the rougher. The tailing from the lead machine is the deleadéd pulp ready for zinc flotation.

At this point the reagents necessary for the flotation of the sphalerite are added, and the pulp is run into the seventh cell of a 10-cell M.S. standard machine ③. The concentrate drawn from the last four cells of this machine is sent to the head of the machine, from which the final zinc concentrate is obtained. Thus the machine is both a rougher and a cleaner, the roughing being done in the last four cells and the cleaning in the first six. The concentrate from the first two cells of the zinc machine are passed on a pilot table ④ to detect any irregularities in operation that would result in galena floating behind schedule in the zinc cells; the lead product obtained on these pilot tables is added to the lead concentrate, and the tailing from the pilot tables is combined with the concentrate drawn from the third to sixth cell

of the zinc flotation machine ③ to form the final zinc concentrate.

The tailing from the zinc flotation machine still contains considerable zinc which can be floated if sufficient contact is allowed for the reagents still in solution to act on the surfaces of the minerals; this is done in Dorr thickeners ⑤, which allow a time of contact of at least 2 hr. and also thicken the pulp to the desired

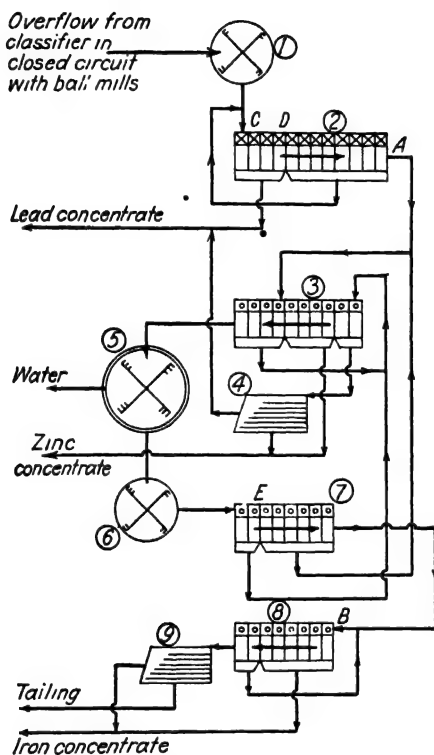


FIG. 65. —Flotation division, Midvale mill.

consistency. Following this conditioning the pulp passes through a Devereux agitator acting as a surge tank ⑥ to the zinc scavenger machine ⑦ which makes a concentrate, a middling, and a tailing. The concentrate from ⑦ is returned to the head of ③; the middling is returned to the head of the same machine ⑦, or more frequently to the seventh cell in ③ together with the new de-leaded pulp.

The tailing from ⑦ is treated for collection of the iron in an eight-cell mechanical-agitation machine ⑧. A finished product

is floated from the first six cells and a middling from the last two. The middling is returned to the head of ⑧. Part of the tailing from ⑧ is passed on pilot tables for visual inspection of the metallurgical results and for the recovery of some additional lead and iron. This is combined with the flotation iron concentrate. It should be noted that the flow-sheet given here is approximately the same for each of the three sections but is changed occasionally to suit the variations in the ore treated.

The reagents used at the Midvale plant and their place of addition are presented in Table 62. The features of the reagent combination used at Midvale are the use of sodium sulfite to inhibit sphalerite and pyrite in the lead circuit, the use of additional sodium sulfite to inhibit the pyrite in the zinc circuit, and the use of sodium sulfide to activate pyrite in the iron circuit. Justification for the use of these reagents has been presented by R. A. Pallanch<sup>(18)</sup>.

TABLE 62.—REAGENTS USED AT MIDVALE

Reagent	Quantity, lb. per ton	Place of addition
Sodium sulfite. ....	1.0	Primary grinding mill (rod mill).
	0.5	To dealed pulp, ahead of seventh cell in zinc rougher <i>A</i> .
Zinc sulfate. ....	0.25 to 1.0	Primary grinding mill (rod mill).
Sodium sulfide . . . . .	0.6	Ahead of iron flotation machine <i>B</i> .
Copper sulfate. . . . .	1 0 to 1.5	To dealed pulp, ahead of seventh cell of zinc rougher <i>A</i> .
Potassium xanthate. . . . .	0.05	Ahead of lead flotation machine <i>C</i> .
	0.10	To dealed pulp, ahead of seventh cell of zinc rougher <i>A</i> .
Cresylic acid. ....	0 01	Ahead of iron flotation machine <i>B</i> .
Oil mixture (80 per cent Republic 19-B; 20 per cent pine oil) . . . . .	0 3 to 0.4	To primary grinding mill.
	0.2	Ahead of fifth cell in lead rougher (lead middling) <i>D</i> .
	0.2	To dealed pulp, ahead of seventh cell of zinc rougher <i>A</i> .
Oil mixture (two-thirds Republic 19-B; one-third Hardwood creosote) . . . . .	0.1	To second zinc middlings <i>E</i> .

Metallurgical results obtained at Midvale are similar to those obtained at other plants treating complex ores. The management of the United States Smelting, Refining and Mining Company has tested the combination of cyanide and zinc sulfate on their ores but has decided to retain the use of sodium sulfite and zinc sulfate.

**The Tooele Mill.**—The Tooele mill of the International Smelting Company, located at Tooele, Utah, treats ores that are similar to those treated at the Midvale mill except that a larger proportion of the simpler Park City ores is treated there. The mill is arranged in two sections so that the Park City ores can be segregated from the Bingham ores. Mill capacity is about 1200 tons daily.

The two sections are similar, yet there are differences in equipment and in the amount of reagents used<sup>(27)</sup>. Figure 66 represents the flotation division of the flow-sheet for one of the sections. The classifier overflow of each section goes to two M.S. flotation machines in parallel ①, each composed of 14 cells actuated by 18-in. full double-disk agitators. These machines make a rougher lead concentrate from the first four to six cells and a middling from the remainder, the middling being returned to the head of the machine. The rougher concentrate is cleaned in one three-pan 3- by 3-ft. Callow cell ② whose tailing is returned to the head of the lead rougher ① and whose concentrate is a finished product going to a 30-ft. Dorr thickener ③, thence to a 12- by 10-ft. Oliver filter ④ for dewatering.

The deleded pulp goes to a 30-ft. Dorr thickener ⑤ for thickening and conditioning prior to zinc flotation, then to four standard M.S. cells ⑥, for further conditioning, no froth being collected from these cells. Zinc flotation is accomplished in four Callow machines in parallel, the first four pans, ⑦, of each machine (of the same type as that used in the lead cleaning) being used to secure a rougher concentrate, and the last four pans, ⑧, to secure a middling which is returned to the thickener ⑤ ahead of the zinc circuit. The rougher zinc concentrate is cleaned in two six-pan Callow cleaners ⑨, whose tailing is returned to the thickener ⑤ ahead of the zinc circuit, and whose concentrate is the finished zinc product. The zinc concentrate is dewatered in a 40-ft. Dorr thickener ⑩, and a 12- by 10-ft. Oliver filter ⑪.

The tailing from the zinc roughers is floated in two 12-pan Callow machines in parallel, the first six pans, ⑫, producing a

rougher iron concentrate, and the last six pans, ⑬, of each machine producing a middling which is returned at the head of the machine. The rougher concentrate is cleaned in one six-pan Callow iron cleaner ⑭, the cleaner tailing being returned to the iron rougher and the cleaner concentrate going to a 30-ft. Dorr

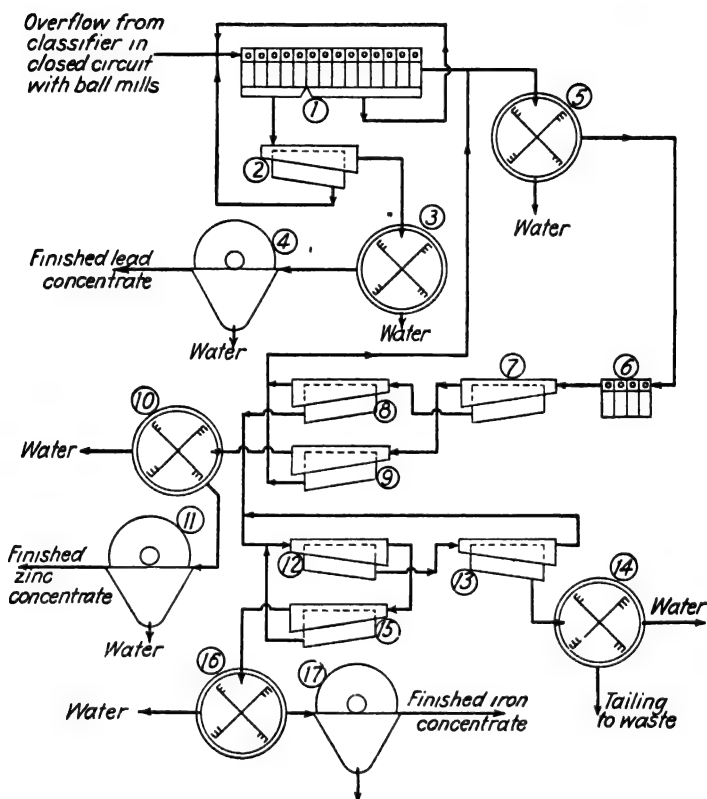


FIG. 66.—Flotation division, Tooele mill.

thickener ⑭ and a 12- by 10-ft. Oliver filter ⑮ for dewatering. The tailing from the iron-flotation rougher is dewatered in a 100-ft. Dorr thickener ⑭. The water secured from all the thickeners is saved because of the scarcity of water.

The reagents used are presented in Table 63. They typify general practice except in two respects: the use of thiocarbonyl in place of xanthate as the major collector in the lead circuit, and the use of aerofloat (dithiophosphoric acid) for the zinc

TABLE 63.—REAGENTS USED AT TOOEE MILL  
(After Young and McKenna.)

Reagent	Amount used, lb. per ton		Place of addition
	Park City ores	Bingham ores	
Sodium carbonate.....	.....	5.0	Ball mills.
Sodium carbonate.....	2.0 to 3.5	.....	Ahead of zinc circuit.
Sodium cyanide.....	0.3 to 0.4	0.2 to 0.3	Ball mills.
Zinc sulfate.....	0.6 to 1.2	0.6 to 1.2	Ball mills.
Copper sulfate.....	0.7 to 1.5	0.7 to 1.5	To tailing from lead rougher.
Thiocarbanilid.....	0 10	0.10	Ball mills.
Potassium ethyl xanthate. {	0.03 to 0.04	0.03 to 0.04	Lead circuit.
	0.03 to 0.04	0.03 to 0.04	Zinc circuit.
	0.15 to 0.25	0.15 to 0.25	Iron circuit.
Aerofloat.....	0.15	0 15	To tailing from lead rougher.

TABLE 64.—GRADES OF PRODUCTS AT TOOEE MILL  
(After Young and McKenna.)

Products	Au, oz. per ton	Ag, oz. per ton	Pb, per cent	Zn, per cent	Fe, per cent	Insol., per cent
Section I (Park City)						
Feed. ....	0 10	8.33	2.9	10.3	9.3	
Lead concentrate. ....	0.787	140.61	65.3	7.1	3.3	2.0
Zinc concentrate . ....	0 10	7 10	0.9	59.1	2.7	1.9
Iron concentrate . ....	0.16	6.64	1.5	4.3	36.9	8.6
Tailing . ....	0.045	1.53	0.2	0.4	8.3	
Section II (Bingham)						
Feed. ....	0.05	5 12	8.6	7.1	10.9	
Lead concentrate. ....	0.10	35.57	66.4	5.6	2.4	2.4
Zinc concentrate. . ....	0.04	2 16	2.7	59.8	1.6	1.9
Iron concentrate. . ....	0 14	6.16	5.0	2.7	34.8	9.3
Tailing. . ....	0.025	0.58	0.4	0.2	10.0	

Note.—Selectivity indices are as follows: Lead-zinc in lead cycle 16.3 (I), 8.3 (II); lead-iron in lead cycle 22.8 (I) 16.2 (II); zinc-iron in zinc cycle 18.9 (I), 36.0 (II).

circuit. Xanthate is the collector in the iron circuit, and an auxiliary collector in the lead and the zinc circuits. The small

## CHAPTER X

### SULFIDE COPPER-ZINC, COPPER-LEAD, AND COPPER-NICKEL ORES

*Copper-zinc ores* are those in which the copper content and the zinc content each form a substantial part of the total value of the ores. Similarly *copper-lead ores* and *copper-nickel ores* are those in which copper and lead or copper and nickel each form a substantial portion of the value of the ores. Ores of these types are generally more complex than is indicated by the simple hyphenated name as they almost always contain a large proportion of iron minerals which are sometimes barren of valuable metals but at other times gold bearing. In this chapter the treatment of copper-zinc, copper-lead and copper-nickel ores will be considered without particular reference to their precious-metal content.

Copper-zinc ores are relatively abundant and many of the massive sulfide deposits in which chalcopyrite is the chief mineral contain zinc. Copper-lead ores are less abundant than copper-zinc ores, and they generally involve a substantial amount of zinc together with the lead, copper, and iron sulfides as well as some silver and gold. They are the most complex of the ores whose treatment by selective flotation has been attempted. Copper-nickel ores occur in few localities and until recently were not treated by flotation.

#### COPPER-ZINC ORES

The problem of separating copper from zinc sulfides resembles the problem of separating lead from zinc sulfides from an economic standpoint as well as from a technical standpoint.

**Economic Features.**—In a copper concentrate, zinc is a worthless diluent for which freight has to be paid, and for which an economic scheme of recovery has yet to be worked out in practice. However, zinc is not harmful to copper smelting in the way in which it is to lead smelting as it is fumed instead of remaining in the slag. Comparing the effects of zinc in a lead



and a copper concentrate, it is therefore clear that zinc is less objectionable and less costly in a copper product than in a lead product.

To the hydroelectrolytic zinc refinery copper in zinc concentrates is worth but a fraction of what it would be worth to a copper smelter. This, because copper must be removed with zinc dust from the pregnant zinc solution and refined following a flow-sheet made complicated by the simultaneous precipitation of cadmium and other minor metals. Even though copper in zinc concentrates is worth much less than in copper concentrates, the cost of recovering it is substantially below its value, so that electrolytic zinc refineries should make a payment for it. The very low copper content of the zinc concentrates made in the United States has not justified this added complication to hydroelectrolytic zinc refinery schedules, but if considerable copper were to find its way in zinc concentrates, it is certain that some sort of payment for it would be made perhaps on the general lines of the allowance for lead that is currently made.

**Technical Features.**—From a technical standpoint the separation of copper sulfides from zinc sulfides is more difficult than the separation of lead sulfides from zinc sulfides. The greater difficulty results from several factors.

1. There may be several copper minerals in an ore but galena is the only lead sulfide of importance.

2. The various copper sulfides are affected to different degrees by the reagents used to separate zinc sulfides from copper sulfides, so that an incomplete recovery of some copper-bearing sulfides may result if zinc sulfide is adequately inhibited.

3. Copper salts activate sphalerite more readily than lead salts; also, copper salts (sulfates) are more likely to occur in copper-zinc ores than lead salts in lead-zinc ores because of the much greater solubility of copper sulfate than of lead sulfate.

4. Iron sulfides are almost always present in large quantity in copper-zinc ores whereas some lead-zinc ores are relatively iron-free.

The most common copper mineral in copper-zinc ores is chalcopyrite. Bornite and chalcocite occur in some copper-zinc ores, as in the Butte district of Montana. The zinc mineral is generally the iron-bearing variety, marmatite. Iron occurs as pyrite and as pyrrhotite. The floatabilities of these minerals have been discussed in Chaps. VIII and IX.

LABORATORY DATA ON THE SELECTIVE FLOTATION OF  
CHALCOPYRITE-MARMATITE ORES

Considerable work on the copper-zinc problem has been done in Canada in view of the abundance of sulfide copper-zinc ores in the Dominion<sup>(2)</sup>. Much of what follows has been abstracted from the work of the Canadian investigators to whom due appreciation for permission to use their data is gratefully recorded.

**An Ore from Rouyn, Quebec.**—Table 65 presents the metallurgical results obtained on an ore<sup>(1)</sup> containing copper, 7.36 per cent; gold, 0.03 oz. per ton; silver, 2.45 oz. per ton; zinc, 6.53 per cent; iron, 35.5 per cent; and insoluble, 18.6 per cent. The minerals in the ore were chalcopyrite, marmatite, pyrite, and pyrrhotite. The reagents used are given in Table 66 and the selectivity indices between chalcopyrite and marmatite in the copper-floating cycle, between chalcopyrite and the iron sulfides in the copper-floating cycle, and between the marmatite and the free-iron sulfides in the zinc-floating cycle in Table 67. In calculating the selectivity indices it was assumed that the copper occurred altogether as chalcopyrite, that the zinc mineral contained 60 per cent zinc, and that half the free iron occurred as pyrite and the other half as pyrrhotite. The copper and zinc concentrates were furthermore assumed to contain 1 to 2 per cent insoluble. The accuracy of the values obtained for the selectivity indices depends to some extent on the exactness of these assumptions; however, most of the indices are probably not in error by as much as 0.5 unit.

Tables 65 to 67 show that very fine results can be obtained on certain copper-zinc ores. In comment of the data presented in these tables it might be remarked that the ore on which the work was done seemed particularly well suited for flotation: the relatively large bulk of chalcopyrite and marmatite (20 and 10 per cent of the total bulk of the ore) permitted the formation of a nice-textured froth, and the bulk of the copper and zinc minerals being fairly close to each other the production of concentrates of suitable grades did not involve undue losses in recovery.

The standard reagents used (Table 66) include sodium carbonate, sodium cyanide, cresylic acid, and pine oil in the copper cycle; copper sulfate, xanthate, and pine oil in the zinc cycle. Comparing tests 2, 5, 9, 10, 11, in which no thiocarbanilid was used with the other tests in which it was used to the extent of 0.20 lb. per ton (except the last test in which 0.25 lb. per ton was used), it is found that the copper-zinc selectivity index

TABLE 65.—METALLURGICAL RESULTS OBTAINED ON A CANADIAN COPPER-ZINC ORE (REAGENTS AS PER TABLE 66)  
(After Godard.)

Test number	Product	Metal content					Recovery, per cent			
		Weight, per cent	Cu, per cent	Zn, per cent	Au, oz per ton	Ag, oz per ton	Cu %	Zn %	Au %	Ag %
1	Cu concentrate	25.6	26.16	3.01	0.08	8.12	93.3	11.3	74.5	83.5
	Zn concentrate	23.2	1.47	25.04	0.03	1.01	4.7	87.2	25.4	9.4
	Tailing	51.2	0.28	0.21	tr.	0.35	2.0	1.5	...	7.1
2	Cu concentrate	30.0	23.08	4.58	0.08	7.60	95.6	20.9	80.0	89.0
	Zn concentrate	20.0	1.01	25.17	0.03	0.75	2.8	76.5	19.9	5.9
	Tailing	50.0	0.23	0.34	tr.	0.20	1.6	2.6	...	5.1
3	Cu concentrate	25.1	26.04	3.63	0.08	7.94	91.4	13.7	50.0	83.0
	Zn concentrate	15.3	2.89	34.88	0.02	1.34	6.2	80.6	7.5	8.5
	Table concentrate	5.5	0.13	0.31	0.11	0.35	0.1	0.3	15.0	0.8
4	Tailing	54.1	0.30	0.67	0.02	0.34	2.3	5.4	27.5	7.7
	Cu concentrate	28.0	23.44	3.43	0.08	7.86	91.8	14.4	72.7	85.2
	Zn concentrate	12.0	2.89	35.19	0.02	1.20	4.9	63.2	7.8	5.6
5	Zn middling	19.8	0.73	6.95	0.01	0.61	2.0	20.6	6.5	4.7
	Tailing	40.2	0.24	0.29	0.01	0.29	1.3	1.8	13.0	4.5
	Cu concentrate	25.6	24.52	3.17	0.08	7.88	88.0	12.1	71.4	80.6
6	Zn concentrate	24.3	2.63	22.27	0.02	1.14	8.9	80.5	17.1	11.1
	Zn middling	17.0	0.63	2.08	tr.	0.55	1.5	5.3	...	3.8
	Tailing	33.1	0.34	0.42	0.01	0.34	1.6	2.1	11.5	4.5
7	Cu concentrate	27.2	25.68	3.06	0.08	8.06	97.0	13.0	60.1	86.8
	Zn concentrate	9.2	1.02	48.71	0.02	1.09	1.3	70.0	5.4	3.9
	Zn middling	6.0	0.66	7.92	0.06	0.94	0.6	7.4	10.9	2.2
8	Tailing	57.6	0.14	1.06	0.01	0.31	1.1	9.0	17.6	7.1
	Cu concentrate	30.2	22.62	4.00	0.08	7.12	95.5	18.5	75.3	88.3
	Zn concentrate	8.5	1.60	46.03	0.02	1.12	1.9	60.1	5.3	3.9
9	Zn middling	13.6	0.81	7.93	0.01	0.52	1.5	16.5	4.4	2.9
	Tailing	47.7	0.17	0.67	0.01	0.25	1.1	4.9	15.0	4.9
	Cu concentrate	28.0	23.74	3.68	0.08	7.04	93.0	16.1	75.4	76.0
10	Zn concentrate	9.8	1.22	47.38	0.01	0.81	1.7	72.9	3.4	3.1
	Zn middling	9.7	1.07	3.68	0.01	0.71	1.4	5.0	3.4	2.3
	Tailing	52.2	0.53	0.65	0.01	0.92	3.9	5.4	17.8	18.6
11	Cu concentrate	27.5	22.88	8.03	0.08	6.40	88.1	34.7	79.2	82.3
	Zn concentrate	9.3	2.87	38.01	0.01	1.11	3.7	55.6	3.2	4.8
	Zn middling	14.5	1.61	2.34	tr.	0.61	3.3	5.3	...	4.1
12	Tailing	48.7	0.72	0.57	0.01	0.39	4.9	4.4	17.6	8.8
	Cu concentrate	29.0	21.73	4.05	0.08	6.06	86.7	17.9	82.3	80.0
	Zn concentrate	12.9	4.39	38.11	0.02	1.56	7.8	75.0	9.2	9.2
13	Zn middling	12.2	1.49	2.49	0.02	0.67	2.5	4.6	8.5	3.7
	Tailing	45.9	0.47	0.35	tr.	0.34	3.0	2.5	...	7.1
	Cu concentrate	29.3	21.22	4.26	0.08	7.68	86.6	19.3	79.0	84.4
14	Zn concentrate	11.4	3.56	40.79	0.01	1.37	5.5	71.9	3.8	5.9
	Zn middling	7.9	2.33	3.68	tr.	1.02	2.6	4.5	...	3.0
	Tailing	51.4	0.74	0.54	0.01	0.35	5.3	4.3	17.2	6.7
15	Cu concentrate	28.2	24.38	3.37	...	...	95.6	14.8	...	...
	Zn concentrate	10.7	1.19	48.41	...	...	1.8	78.3	...	...
	Zn middling	11.1	0.90	3.32	...	...	1.4	5.7	...	...
16	Tailing	50.0	0.17	0.16	...	...	1.2	1.2	...	...
	Cu concentrate	32.1	21.80	3.32	...	...	97.0	16.2	...	...
	Zn concentrate	16.2	0.55	31.62	...	...	1.2	77.7	...	...
17	Zn middling	18.6	0.39	1.45	...	...	1.0	4.1	...	...
	Tailing	33.1	0.18	0.39	...	...	0.8	2.0	...	...

averages 5.9 for the tests with no thiocarbanilid and 10.2 for those with thiocarbanilid. If tests 1 and 2 are excluded on account of the use of xanthate (jointly with thiocarbanilid in test 1 and singly in test 2), the selectivity indices average 10.2 for the tests with thiocarbanilid and 5.2 for the tests without thiocarbanilid. Since the deviations of individual selectivity

TABLE 66.—REAGENTS USED ON A CANADIAN COPPER-ZINC ORE (METALLURGICAL RESULTS,  
TABLES 65 AND 67)  
(After Godard.)

Reagent	Amount added, lb. per ton												
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 12	Test 13
To ball mills													
Sodium carbonate	5 0	2 0	5 0	2 0	2 0	4 0	4 0	4 0	4 0	5 0	5 0	5 0	5 0
Sodium cyanide	0 40	...	0 20	0 50	0 50	0 30	0 30	0 30	0 30	0 20	0 20	0 35	0 35
Lime	0 20	1 5	...	2 0	2 0	...	...	...	...	...	...	0 20	0 25
Thiocarbamid	...	...	0 08	...	...	...	...	...	...	...	0 30	...	...
Water-gas tar	...	...	...	...	...	...	...	...	...	...	...	...	...
Coal tar	...	...	...	...	...	...	...	...	...	...	...	...	...
Coal-tar creosote	...	...	...	...	...	...	...	...	...	...	...	...	...
Barrett No. 4	...	...	...	...	0 40	...	...	...	...	...	...	...	...
Crealytic acid	...	...	0 04	...	...	...	...	...	...	...	...	...	...
Copper sulfate	...	0 20	...	...	...	...	...	...	...	...	...	...	...
Potassium ethyl xanthate	0 20	0 20	...	...	...	...	...	...	...	0 08	0 08	0 08	0 08
Pine oil	0 05	0 08	...	0 08	0 05	0 08	0 08	...	0 08	0 08	0 08	0 04	0 04
Crealytic acid	...	...	...	...	...	...	...	...	...	...	...	...	...
Sodium carbonate	...	...	...	...	...	...	...	...	...	...	...	...	...
Sodium hydroxide	...	0 6	...	...	...	3 0*	...	...	...	...	...	...	...
Lime	...	...	...	...	...	...	5 0*	...	...	...	...	...	...
Copper sulfate	2 0	2 0	2 0	2 0	...	1 5	...	1 5	1 5	1 5	1 5	1 5	1 5
Potassium ethyl xanthate	0 20	0 40	0 20	0 30	0 30	0 30	0 30	0 30	0 35	0 30	0 40	0 25	0 30
Barrett No 634	...	...	...	...	...	...	...	...	...	...	...	...	...
Pine oil	0 05	0 08	0 08	0 08	0 08	0 08	0 08	0 08	0 08	0 08	0 08	0 04	0 04
To zinc cells													
Grind to	100 mesh	200 mesh	150 mesh	150 mesh	150 mesh	†	†	150 mesh	150 mesh	150 mesh	200 mesh	150 mesh	200 mesh

\* Added to regrinding ball mill  
† 100 mesh for copper "float"; 200 mesh for zinc float

TABLE 67.—SELECTIVITY INDICES OBTAINED IN THE SELECTIVE FLOTATION OF A CANADIAN COPPER-ZINC ORE (SEE ALSO TABLES 65 AND 66)

Test number	In copper cycle		In zinc cycle
	Copper to zinc	Copper to free iron	Zinc to free iron
1	10.4	11.7	13.0
2	9.1	11.5	9.9
3	8.2	10.3	11.3
4	8.2	8.4	5.7
5	7.3	7.9	5.3
6	14.7	16.7	11.7
7	9.7	10.8	9.2
8	8.3	9.3	13.5
9	3.7	8.0	10.1
10	5.5	5.7	12.1
11	5.2	5.5	11.9
12	10.9	12.4	18.5
13	12.9	11.8	8.0

indices from the mean are small, it may be considered as conclusive for the ore under consideration that thiocarbanilid caused a better copper-zinc separation than oils. Unfortunately, insufficient data are available to compare the effectiveness of thiocarbanilid and xanthate. In the same way as thiocarbanilid assists in magnifying the selectivity index between copper and zinc, it increases the selectivity index between chalcopyrite and the free-iron sulfides from 6.0 to 11.1. Although cyanide was used consistently, its omission in test 2 did not preclude a good rejection of the zinc and iron from the copper concentrate.

**A British Columbia Ore.**—Table 68 presents the metallurgical results obtained on a copper-zinc ore<sup>(5)</sup> very different from the ore covered by the tests presented in Tables 65 to 67. Table 69 is a record of the reagents used, place of addition, and fineness of grinding.

The ore was very low in copper (chalcopyrite), the zinc occurred as iron-free sphalerite, and there were little pyrite and pyrrhotite. In respect to the production of a high-grade zinc product this ore was much easier to handle than the ore of Tables 65 to 67; in respect to making a satisfactory copper product it was more difficult, particularly if a substantial recovery of copper had to

TABLE 68.—METALLURGICAL RESULTS OBTAINED ON A LOW-COPPER,  
HIGH-ZINC CANADIAN COPPER-ZINC ORE.  
(After Parsons.)

Test number	Product	Weight, per cent	Metal content,		Recovery, per cent		Copper-zinc selectivity index in copper cycle
			Cu, per cent	Zn, per cent	Cu	Zn	
1	Copper concentrate	6.2	10.14	35.7	82.0	12.0	5.8
	Zinc concentrate	34.8	0.3	46.5	13.5	87.0	
	Tailing	59.0	0.06	0.36	4.5	1.0	
2	Copper concentrate	1.5	24.94	16.9	50.8	1.4	7.4
	Copper middling	1.3	5.37	31.95	9.4	2.2	
	Zinc concentrate	35.0	0.60	48.84	28.2	93.7	
3	Tailing	62.2	0.14	0.78	11.6	2.6	7.4
	Copper concentrate	5.2	11.16	23.28	79.8	6.7	
	Zinc concentrate	33.9	0.35	48.98	16.1	91.6	
4	Tailing	60.9	0.05	0.51	4.1	1.7	6.6
	Copper concentrate	8.3	7.56	17.88	78.9	8.0	
	Zinc concentrate	34.2	0.39	49.45	16.7	91.0	
5	Tailing	57.5	0.06	0.33	4.4	1.0	4.0
	Copper concentrate	12.4	5.22	39.91	85.5	26.8	
	Zinc concentrate	32.4	0.22	41.04	9.4	72.2	
6	Tailing	55.2	0.07	0.33	5.1	1.0	5.4
	Copper concentrate	5.3	9.5	20.45	67.0	6.5	
	Zinc concentrate	31.9	0.68	48.45	28.8	92.0	
7	Tailing	62.8	0.05	0.41	4.2	1.5	6.5
	Copper concentrate	5.5	8.86	15.93	67.2	4.6	
	Zinc concentrate	37.7	0.57	47.21	29.7	94.3	
8	Tailing	56.8	0.04	0.36	3.1	1.1	8.2
	Copper concentrate	3.2	17.22	20.07	70.7	3.5	
	Zinc concentrate	31.5	0.56	54.68	22.6	94.3	
9	Tailing	65.3	0.08	0.62	6.7	2.2	9.5
	Copper concentrate	2.8	17.30	13.72	65.9	2.1	
	Copper middling	2.9	0.72	18.84	2.9	3.0	
	Zinc concentrate	35.9	0.59	47.51	28.9	93.0	
	Tailing	58.4	0.03	0.61	2.3	1.9	

NOTE.—In test 9, the copper concentrates from four lots of 1000 g. each were combined and reground to -200 mesh before cleaning.

be made to justify the separation economically. In this instance the chalcopyrite:sphalerite ratio was 1:13 instead of 2:1.

The reagent combinations used in the tests on this ore were about the same as those used on the high-copper ore previously

TABLE 69.—REAGENTS USED IN THE SELECTIVE FLOTATION OF A LOW-COPPER, HIGH-ZINC CANADIAN COPPER-ZINC ORE  
(After Parsons.)

Reagent	Amount added, lb. per ton								
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
To ball mill	Sodium carbonate	6 0	...	...	3 0	5 0	5 0	4 0	3 0
	Lime	...	...	4 0	...	0 30	0 30	0 20	0 20
	Sodium cyanide	0 20	0 20	0 25	0 25	...	1 5	1 0	0 8
	Zinc sulfate	...	...	...	...	0 10	...	...	...
	Thiocarbamid	0 20	0 20	...	...	...	0 20	...	0 20
	Water-gas tar	...	...	...	...	...	0 08	...	0 08
To copper cells	Crealyic acid	...	...	...	...	...	...	...	...
	Potassium ethyl xanthate	...	...	0 15	0 10	...	...	0 10	...
	Pine oil	0 10	0 05	...	0 04	...	0 04	0 04	0 04
To zinc cells	Crealyic acid	...	...	0 12	...	0 08	...	...	...
	Copper sulfate	1 15	1 15	2 0	2 0	2 0	2 0	2 0	2 0
	Potassium ethyl xanthate	0 30	0 30	0 6	0 6	0 6	0 6	0 6	0 5
To regrinding rougher concentrate	Pine oil	...	0 05	0 04	0 04	0 04	0 04	0 04	0 04
	Lime	...	...	...	...	...	...	...	0 40
	Sodium cyanide	...	...	...	...	...	...	...	0 05
	Thiocarbamid	...	...	...	...	...	...	...	0 03
Grind to	100 mesh	100 mesh	150 mesh	200 mesh	200 mesh	200 mesh	200 mesh	100 mesh	150 mesh

discussed. One feature worthy of comment is the fact that grinding the rougher copper concentrate with zinc-inhibiting agents allows the production of a cleaner copper concentrate with the loss of but a small portion of the copper (test 9).

**A Manitoba Ore.**—The tests discussed so far were batch tests. The results of one locked-batch test are given by C. S. Parsons<sup>(6)</sup> (Table 70). The ore was ground with lime, 3.0 lb. per ton; then

TABLE 70.—METALLURGICAL RESULTS OF A LOCKED-BATCH TEST  
ON A CANADIAN COPPER-ZINC ORE  
(After Parsons, 1927.)

Product	Metal content					Recovery, per cent					Copper-zinc selectivity index
	Cu, per cent	Zn, per cent	Pb, per cent	Au, oz. per ton	Ag, oz. per ton	Cu	Zn	Pb	Au	Ag	
Feed.....	1 89	4.61	0.45	0.10	1.36						
Copper concentrate	17 0	3.0	4.4	0.53	4.90	83.0	6 0	90 0	48 5	33 1	8.5
Zinc concentrate	1.1	43.5	0.0	0.03	1 6	5.0	83 2	0	26.4	10 4	
Tailing.....	0.28	0.6	0.05	0.06	0.94						

agitated with salt, 1.0 lb. per ton, for 3 min. A copper concentrate was obtained by adding xanthate, 0.12 lb. per ton, and pine oil, 0.04 lb. per ton. The rougher copper concentrate was cleaned with salt, 0.5 lb. per ton; xanthate, 0.02 lb. per ton; and pine oil, 0.04 lb. per ton. Locking of the tests was obtained by adding the cleaner tailing to the next charge of ore. The decoppered pulp was floated for zinc with lime, 1.0 lb. per ton; copper sulfate, 0.25 lb. per ton; xanthate, 0.12 lb. per ton; and cresylic acid, 0.04 lb. per ton. The zinc concentrate was cleaned with copper sulfate, 0.1 lb. per ton; lime, 1.0 lb. per ton; and xanthate, 0.02 lb. per ton. The cleaner tailing was joined to the decoppered pulp of the subsequent test.

The results show gratifying extractions of copper in the copper concentrate and of zinc in the zinc concentrate, but the grade of the zinc concentrate is hardly satisfactory.

In comment of the reagent additions it might be said that the practice of adding collecting and frothing agents to cleaning operations has fallen in disuse as better results are generally obtained through cleaning with no additional reagents whatever, or by adding inhibiting reagents only. Also, evidence is lacking that salt has any direct beneficial action.



**Amulet Ore.**—Parsons and Anderson<sup>(7)</sup> report some results obtained on large-scale pilot-plant tests on a carload of copper-zinc ore from the Amulet mine in the Rouyn district of Quebec. The ore was made up of chalcopyrite and marmatite in an iron sulfide gangue containing a large proportion of pyrite; the ore was substantially oxidized due to standing in a partly ground condition and contained a large amount of soluble salts, particularly sulfates (equivalent to 9.0 lb. of sulfuric acid per ton of ore).

One of the tests (number 8 of Parsons and Anderson) is typical of the results obtained. The ore was crushed to four mesh and fed by a belt conveyor to a ball mill in closed circuit with a classifier. The classifier overflow went to an eight-cell mechanical agitation machine which produced a copper concentrate. The first three cells produced a finished concentrate and the last five a middling, returned to the ball mill for further grinding. The tailing from the copper cells went to an air lift with a large well which was built for this particular test in order that a certain time of contact be had by the pulp with copper sulfate before entering the zinc flotation cells. The zinc was floated in a set of Callow pneumatic cells, the rougher concentrate being cleaned twice, and the cleaner and recleaner tailings being returned to the rougher cells with the feed. The ore was fed at the rate of 772 lb. per hour for 7 hr.

Table 71 records the average amount of each reagent that was added during a 3-hr. sampling period, as well as the place of

TABLE 71.—REAGENTS ADDED IN PILOT-PLANT FLOTATION OF A SLIGHTLY WEATHERED HIGH-IRON COPPER-ZINC ORE FROM THE AMULET MINE

(After Parsons and Anderson.)

<b>Copper Reagents</b>	
Sodium carbonate.	13. lb. per ton, added in dry state to ball mill
Sodium cyanide.	0.30 lb. per ton, added to ball-mill discharge ahead of Dorr classifier
Zinc sulfate.	0.57 lb. per ton, added to ball-mill discharge immediately after cyanide addition
Aerofloat No. 15.	0.045 lb. per ton, added to first copper flotation cell
<b>Zinc Reagents</b>	
Copper sulfate.	2.1 lb. per ton, added to air-lift between copper and zinc circuits
Ethyl xanthate.	0.28 lb. per ton, added to air-lift after the copper sulfate, and separately from the copper sulfate
Pine oil	Occasional additions of small amounts to increase frothing

addition of the reagents. Table 72 records the metallurgical results obtained during the run. The effectiveness of the copper-

TABLE 72.—METALLURGICAL RESULTS OBTAINED IN PILOT-PLANT FLOTATION OF A SLIGHTLY WEATHERED HIGH-IRON COPPER-ZINC ORE FROM THE AMULET MINE ORE  
(After Parsons and Anderson.)

Product	Metal content				Approximate recoveries		Copper-zinc selectivity index
	Cu, per cent	Zn, per cent	Au, oz. per ton	Ag, oz. per ton	Cu, per cent	Zn, per cent	
Feed .....	3.85	3 25	0 24	3.28			
Copper concentrate..	21 66	9 56	0 82	12 54	91.2	16.7	7.2
Decoppered pulp.....	0 40	8 70	0 04	1 44			
Zinc concentrate..	1 07	52.86	0 06	1 32	3 0	61.3	
Tailing. ....	0 36	2 98	0 05	1 40			

zinc separation was about the same in this test as in the batch tests recorded above. However, the zinc recovery in the zinc concentrate was rather low; this was caused in no small part by the high iron content of the ore, which precluded the production of a zinc concentrate of adequate grade at the same time as a high recovery.

#### PRACTICE IN THE TREATMENT OF CHALCOPYRITE-MARMATITE ORES

Five mills have been operating for some time, one in eastern Canada, one in the eastern United States, one in Japan and two in Manitoba. Another plant is contemplated in Arizona. In each instance the mineral association is chalcopyrite-marmatite-pyrite-pyrrhotite.

**Sherritt-Gordon Pilot Mill.**—Typical results<sup>(8)</sup> from the Sherritt-Gordon ore of Manitoba are presented in Table 73, the reagents used being as per Table 74.

Figure 67 shows the flow-sheet of the pilot mill. After grinding in a rod mill-classifier closed circuit ①, ②, the pulp was conditioned for 30 min. in a conditioning tank ③, then floated in the last six cells of an eight-cell standard M.S. machine ④, of which the first two cells acted as mixing cells. The concentrate was

cleaned in a three-cell Denver sub-aeration machine ⑤ whose concentrate was the finished copper product and whose tailing was returned to the head of the rougher.

The decoppered pulp was floated for zinc in a six-cell Denver sub-aeration cell ⑦ after 30-minutes' conditioning in tank ⑥. The zinc concentrate was cleaned in a small Callow cell ⑧ yielding a finished zinc concentrate and a middling returned at the head of the zinc rougher.

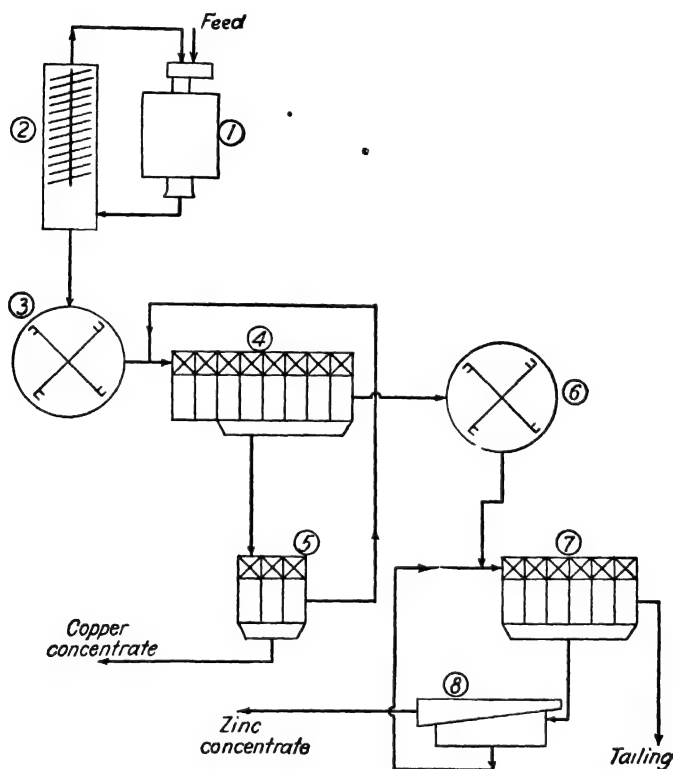


FIG. 67.—Flotation division, pilot mill for treatment of Sherri-Gordon ore.

A pH of 8 to 9 is recommended for the copper circuit.

The joint use of sodium cyanide and copper sulfate for zinc flotation may appear a mistake, because of the mutual consumption of these reagents; however, its value may be explained as follows: since the cyanide was added some time ahead of the copper sulfate, time was afforded for cyanide to react with and

TABLE 73.—PILOT-PLANT METALLURGICAL RESULTS FROM SHERRITT-GORDON ORE  
(After Parsons.)

Product	Grades				Recoveries, per cent			
	Cu, per cent	Zn, per cent	Au, oz. per ton	Ag, oz. per ton	Cu	Zn	Au	Ag
Feed.. . . .	2.00	5.51	0.04	0.48				
Copper concentrate . . .	17.7	3.62	0.16	3.50	92.5	6.9	64	80.0
Zinc concentrate. . .	0.63	36.3	0.01	0.27	4.0	88.6	4	9.8
Tailing . . .	0.08	0.33	0.01	0.07	3.5	4.5	32	11.1

Copper-zinc selectivity index, 12.8

TABLE 74.—REAGENTS USED IN SHERRITT-GORDON PILOT-MILL WORK  
(After Parsons.)

Added to	Reagents	Lb. per ton
Ball mill.. . . .	{ Sodium carbonate	4 6
	{ Thiocarbamilid	0 14
	{ Sodium cyanide	0 4
Copper-flotation cells. . . .	Cresylic acid	0 56
Zinc-flotation conditioning tank	Sodium cyanide	0 28
Zinc-flotation cells. . . .	{ Copper sulfate	1 25
	{ Potassium ethyl xanthate	0 05

further inhibit the pyrite before copper sulfate was added to activate marmatite in preference to pyrite.

**Flin Flon Plant**<sup>(10)(3)</sup>.—The Hudson Bay Mining and Smelting Company has in operation a concentrator for the treatment of the ores from the Flin Flon mine. The Flin Flon ore bodies contain both disseminated and massive sulfides requiring somewhat different treatment.

Tables 75 and 76 give the metallurgical results and reagent consumption during an 8-day pilot-plant run (25 tons per day) and Figs. 68 and 69 the proposed flow-sheets for the treatment of the two types of ore.

The flow-sheets for the disseminated and massive ore differ in two respects:

TABLE 75.—METALLURGICAL RESULTS DURING AN 8-DAY PILOT RUN  
(OCT. 24 TO 31, 1927) AT FLIN FLON MILL  
(After Phelan.)

Product	Grades				
	Au, oz. per ton	Ag, oz. per ton	Cu, per cent	Zn, per cent	Insoluble, per cent
Heads (calculated) . . . . .	0 043	0.67	2.44	4.25	
Talc product . . . . .	0 010	0.37	0.69	0.80	
Copper concentrate . . . . .	0.190	2.55	13.70	3.50	16.60
Zinc concentrate . . . . .	0.052	1.22	1.85	40.40	2.10
Tailing . . . . .	0 028	0.36	0.42	0.60	
Recoveries, per cent					
	Au	Ag	Cu	Zn	
Talc product . . . . .	1.9	4.8	2.6	1.7	
Copper concentrate . . . . .	52.7	48.1	79.6	11.7	
Zinc concentrate . . . . .	8.2	13.7	6.2	77.2	
Tailing . . . . .	37.3	33.3	11.6	9.4	

Copper-zinc selectivity index in copper circuit, 5.8.

1. The minerals in the sulfide ore are more intimately associated, requiring regrinding of middlings whereas middling regrinding is not necessary in the case of the disseminated ore.

2. The sulfide ore contains a substantial amount of gold and silver that is not recovered by flotation. Cyanidation of the flotation tailing with cyanide regeneration are therefore contemplated.

From the classifiers, the disseminated-ore pulp (Fig. 68) flows into a surge tank ① whence it is fed by a pulp distributor ② to four 24-in., 14-cell sub-aeration talc roughers ③ which make a rougher talc concentrate and a tailing. The rougher talc concentrate is cleaned in four 24-in., seven-cell sub-aeration machines ④.

The detailed tailings from ③ and ④ are fed to four 24-in., 13-cell copper roughers ⑤ which make a finished concentrate from the first four cells and a middling from the last nine. The copper middling is cleaned in four 24-in., three-cell cleaners ⑥ whose tailing is returned to the head of ⑥ by way of a surge tank ⑦ and a pulp distributor ⑧. The concentrate from ⑥

is a finished copper concentrate and joins the concentrate from the first four cells of (5).

The tailing from (5) goes to two flotation machines in parallel used as conditioners (9) one of which has six cells and the other four. From the zinc conditioners the decoppered pulp goes to two 12-cell zinc roughers (10) whose first seven cells make a rougher concentrate and whose last five cells make a middling returned

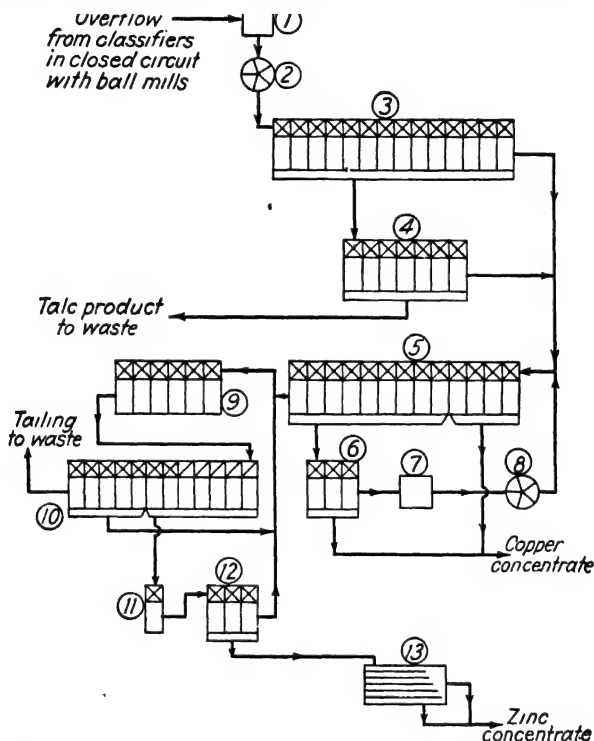


FIG. 68.—Flotation division, Flin Flon mill (disseminated ore).

to the head of (9). The rougher zinc concentrate is conditioned shortly in two one-cell flotation machines in parallel (11) feeding one three-cell and one four-cell zinc cleaner (12). These cleaners make a finished zinc concentrate and a middling which is returned to the head of (9). The finished zinc concentrate is passed over a pilot Wilfley table (13).

The flow-sheet for the heavy sulfide (Fig. 69) follows the same general steps as the flow-sheet for the disseminated ore. That is, there are three flotation cycles: (1) talc flotation, (2) copper



to a cyanide plant for extraction of the precious metals associated with the pyrite.

The ratio of zinc flotation area to copper flotation area is larger for the treatment of the massive-sulfide ore than for the treatment of the disseminated-sulfide ore in accordance with the ratio of the two metals in the two types of ore.

The most remarkable feature about the Flin Flon ore treatment is perhaps the talc flotation ahead of copper and zinc flotation.

TABLE 76.—AVERAGE REAGENT CONSUMPTION (POUNDS PER TON)  
DURING 8-DAY PILOT RUN (OCT. 24 TO 31, 1927) AT FLIN FLON  
MILL  
(After Phelan.)

Reagents Added at primary Ball Mills	
Lime.....	1.66
Zinc oxide.....	0.83
Reagents Added for Talc Flotation	
Pine oil . . . . .	0.05
Reagents Added for Copper Flotation	
Aerofloat....	0.13
Potassium ethyl xanthate .	0.06
Salt (sodium chloride)....	2.05
Potassium ethyl xanthate .	0.055
Zinc sulfate.....	0.54
Reagents Added for Zinc Flotation	
Potassium ethyl xanthate .	0.05
Copper sulfate.....	0.71
Cresylic acid.....	0.08
Potassium ethyl xanthate .	0.06
Copper sulfate.....	0.19
Lime.....	2.34
Lime.....	0.65

at copper conditioner  
at No. 6 copper rougher  
at copper cleaner  
at zinc conditioner  
at zinc rougher  
at zinc cleaner

NOTE:—pH in copper circuit 10.0–11.0 (calculated from “free CaO” determinations).

pH in zinc rougher circuit  $11.9 \pm 0.2$  (calculated from “free CaO” determinations).

pH in zinc cleaner circuit  $12.2 \pm 0.1$  (calculated from “free CaO” determinations).

It was found that a good grade of copper concentrate could not be made if this “talc” was not first removed, because of the great tendency for the fine flakes of some secondary silicates, lumped under the name of “talc,” to report in the concentrate. Pine oil is sufficient to float this talc. The nature of this phenomenon is not definitely known. It should perhaps be regarded as a mechanical overflow of the finer particles in the pulp,



similar to that which would be obtained by elutriating at a very fine size.

The addition of lime and zinc oxide to the primary ball mills and of some lime to the talc cleaner (Table 77) results in substantial inhibition of all the sulfides in the talc-floating stage.

TABLE 77.—REAGENT CONSUMPTION (POUNDS PER TON) AT FLIN FLON MILL (1929)  
(After Phelan.)

Reagents Added at Primary Ball Mills (Massive Sulfide Ore)

Lime..... 1.5

ZnSO<sub>4</sub> ..... 1.06

Reagents Added at Talc-floating Cycle

Pine oil..... 0.03, cell No. 1, rougher

Pine oil. . . . . 0.03, cell No. 4, rougher

Lime. . . . . 0.10, cell No. 1, cleaner

Reagents Added at Copper-floating Cycle

Aerofloat. . . . . 0.066, cell No. 1, rougher

Zinc sulfate . . . . . 0.27, cell No. 1, cleaner

Reagents Added at Zinc-floating Cycle

Copper sulfate . . . 1.00, cell No. 1, rougher conditioner

Lime..... 2.00, cell No. 3, rougher conditioner

Cresylic acid. . . . 0.25, cell No. 4, rougher conditioner

Xanthate. . . . . 0.04, cell No. 4, rougher conditioner

Copper sulfate . . . 0.15, cell No. 10, rougher

Cresylic acid. . . . 0.10, cell No. 10, rougher

Lime. . . . . 0.04, cleaner conditioner

Copper sulfate . . . 0.20, cleaner conditioner

Zinc inhibition apparently does not require cyanide. This is perhaps to be correlated with the very fresh character of the ore and to the absence of secondary enrichment. Zinc oxide which is added to the ball mills takes the place of the conventional zinc sulfate, and at the same time provides some alkalinity, instead of acidity; its use in place of zinc sulfate reduces the lime consumption.

Copper flotation is obtained through the use of aerofloat (Table 77) or aerofloat with xanthate and salt (Table 76). The function of salt is not known, but since its use has been discontinued it may be inferred that salt is not essential. Zinc sulfate is added to the copper cleaners for inhibition of marmatite particles which had inadvertently reported in the rougher copper concentrate. Zinc oxide could hardly be used at this stage without considerable conditioning.

Zinc flotation is attained through the use of the conventional reagents. Double conditioning, one before roughing and one

before cleaning, are featured (Table 77). Considerable lime is added to inhibit the iron, some lime being added before roughing and some before cleaning. \*

The pH is lower in the copper than the zinc circuit. For the test period covered by Table 76, the pH in the copper circuit was in the vicinity of 10 to 11, but in the zinc circuit it was about 12.

Metallurgical results indicate that the metal losses in the talc product are small, indeed.

The copper-zinc selectivity index in the copper circuit was 5.8. No data are available for the zinc-iron index.

**An Arizona Plant.**—Recently a copper-zinc ore body of substantial magnitude was discovered in north-central Arizona. Extensive pilot-plant tests have been conducted on this ore. The principal minerals are pyrite, marmatite (90 per cent ZnS, 10 per cent FeS), and chalcopyrite. A great deal of the marmatite from certain sections of the ore body is naturally activated by the deposition of films of chalcocite and covellite. The extent of this activation is relatively large and considerable difficulty is encountered in deactivating the marmatite.

Chalcopyrite and marmatite are disseminated through the pyrite in an extremely fine state of division. Likewise, pyrite inclusions occur within chalcopyrite and marmatite. This necessitates very fine grinding to liberate the minerals.

Typical metallurgical results are presented in Table 78.

TABLE 78.—METALLURGICAL RESULTS IN THE FLOTATION OF AN ARIZONA COPPER-ZINC ORE

Product	Assays, per cent				Recoveries, per cent		
	Copper	Zinc	Sulfur	Pyrite *	Chalco- pyrite	Mar- matite	Pyrite
Feed. . . . .	0.60	7.0	41.9				
Copper concen- trate . . . . .	8.0	7.5	42.0	64	56	4.5	3.4
Zinc concentrate	1.2	54.0	33.0	3.5	21	83.5	0.5
Tailing . . . . .	0.16	1.0	41.5	87.5	23	12	95.9

#### Selectivity Indices

Copper-zinc in copper cycle, 5.2.

Copper-pyrite in copper cycle, 6.0.

Marmatite-pyrite in zinc cycle, 36.5.

\* Calculated

They indicate a remarkable selection of marmatite from pyrite in the zinc cycle, but a relatively poor selection of chalcopyrite from the other two sulfides. This is perhaps because the rougher zinc concentrate is reground to pass a 300-mesh screen in comparison with the grind of 80 per cent -300 mesh which is used on the feed.

TABLE 79.—REAGENTS USED IN THE FLOTATION OF AN ARIZONA COPPER-ZINC ORE

Cycle	Reagent	Amount of reagent, lb. per ton	Added to
Copper flotation	Lime	5.0 to 7.0	Ball mill
	Sodium cyanide	0.2 to 0.5	Ball mill
	Zinc sulfate	0.6 to 1.5	Ball mill
	Amyl xanthate	0.02 to 0.05	Copper cells
	Pine oil	0.03 to 0.07	Copper cells
Zinc flotation...	Lime	1.0 to 3.0	Zinc conditioners
	Copper sulfate	1.0 to 3.0	Zinc conditioners
	Amyl xanthate	0.08 to 0.15	Rougher zinc cells
	Sodium ethyl dithio-phosphate	0.05 to 0.12	Rougher zinc cells
	Pine oil	0.02 to 0.08	Rougher zinc cells
	Sodium bichromate	0.05	Cleaner zinc cells

Reagents used are as per Table 79. Close alkalinity control, particularly in the copper circuit, is desirable. Alkalinity of 0.02 to 0.10 lb. CaO per ton of water (pH 10.6 to 11.3) is maintained in the copper circuit and of 0.2 to 0.7 lb. CaO (pH 11.6 to 12.2) in the zinc circuit. A somewhat lower alkalinity (0.02 to 0.20 lb. CaO or pH 10.6 to 11.6) is permissible in the zinc cleaners and recleaners. Necessity for maintaining the pH in the copper circuit within narrow limits is due to the fact that if the pH is made higher the copper concentrate contains more marmatite (due to the relatively greater inhibition of chalcopyrite than of activated marmatite by high alkalinity); and that if the pH is made lower, the pyrite is not sufficiently inhibited.

Cyanide and zinc sulfate are necessary to deactivate the naturally-activated marmatite.

Amyl<sup>(9)</sup> xanthate is the base and most important collector used, in both zinc and copper circuits. It has been found, however, that sodium aerofloat in addition to amyl xanthate in the zinc circuit raises extraction

with no sacrifice in grade of concentrate. The amyl-aerofloat quantities are changed to suit froth conditions, maintaining a constant quantity of total collector. The amyl xanthate is a powerful flocculator and the aerofloat a weak flocculator on these ores, hence froth characteristics are controlled to a large extent by the "juggling" of these reagents. It is noteworthy that the relatively large quantity of collector used is more or less a function of the fine grind—(all -200, 80 per cent -300 mesh, and rougher concentrate reground all -300 mesh); when coarser grinds are made, the quantity of collector must be cut to avoid a dead, over-flocculated froth.

Sodium bichromate is used to clean the rougher zinc concentrate, possibly by assisting in the oxidation of pyrite by atmospheric oxygen.

Atmospheric oxygen has been found to be one of the most important modifying reagents. Its function is primarily to depress pyrite, and possibly to promote marmatite, by preparing its surface for reaction with  $\text{CuSO}_4$  and xanthate. It has been found necessary to make a quick float in the copper section—the longer the time here, the more zinc floats with the copper. In the zinc section, on the contrary, the longer the time of contact with air, in conditioners, cells, regrind mill, etc., the better the results, both in extraction and in grade of concentrate. Thirty minutes' conditioning with air is done prior to zinc flotation; the pulp is in the rougher cells about 45 min.; the rougher concentrate is then reground to -300 mesh in a tube mill, emerging at a temperature of about 55°C. This product is then cleaned, recleaned, and re-recleaned. The regrinding of rougher concentrate is almost as important from the standpoint of selective oxidation as from that of unlocking mineral. It has been found that equal metallurgical results can be obtained, if cleaner tail is reground, instead of rougher concentrate, provided the rougher concentrate is conditioned with air (and an oxidizer, such as  $\text{Na}_2\text{Cr}_2\text{O}_7$ ) for a period exceeding 3 hr.

**Ikuno Concentrator, Japan**<sup>(11)</sup>.—At Ikuno mine the essential minerals are chalcopyrite and sphalerite associated with galena, pyrite, and arsenopyrite accompanying quartz and calcite as gangue. The country rock is chiefly liparite.

The crude ores are separated into two classes, one rich in copper which is treated as a simple copper ore, the other rich in zinc which is treated by selective flotation for the production of a copper concentrate and a zinc concentrate.

Figure 70 is a flow-sheet of the flotation division used in the treatment of the copper-zinc ore. After coarse grinding, wash-



The concentrate from ⑤ is treated for the extraction of some galena by tabling, the pulp being fed by a four-way pulp distributor ⑨ to four No. 12 Wilfley tables in parallel ⑩. The tailing from ⑩ which is a product high in copper is again de-leaded in four James tables ⑬, thickened in a 30-ft. Dorr tank ⑭, and filtered in an 8- by 9-ft. Oliver filter ⑮. The concentrate from ⑩ and ⑬ is dewatered in a small settling tank and shipped as lead concentrate.

The decoppered pulp is thickened in a 30-ft. Dorr thickener ⑯, conditioned ⑰, and floated for zinc in eight M.K. cells arranged as in the copper circuit. The concentrate from ⑱ is cleaned in an 18-ft. Forrester cleaner whose first section makes a final concentrate and whose second section makes a cleaner concentrate returned to the head of the machine and a cleaner tailing returned to thickener ⑰. The final concentrate is dewatered in a 30-ft. Dorr thickener ⑳ and a 6- by 7-ft. Oliver filter.

The reagents employed involve lime, zinc sulfate, camphor oil, and xanthate which are used in the copper circuit; and bleaching powder, copper sulfate, xanthate, and camphor oil in the zinc circuit. Lime and zinc sulfate inhibit the sphalerite which is later activated by bleaching powder (to oxidize copper minerals remaining in the decoppered pulp thereby forming cupric ion) and copper sulfate. Camphor oil is a frother similar to pine oil. In Japan it is cheaper than pine oil, just as eucalyptus oil is cheaper in Australia.

Metallurgical results are presented in Table 80.

TABLE 80.—METALLURGICAL RESULTS AT COPPER-ZINC SECTION OF IKUNO CONCENTRATOR (JAPAN)

Product	Metal content				Weight, tons per month	Recovery, per cent			
	Ag, grams per ton	Cu, per cent	Pb, per cent	Zn, per cent		Ag	Cu	Pb	Zn
Feed.....	118	1.55	1.33	8 24	4520				
Copper concentrate	695	13.9	9.12	20.75	393.5	51.2	78.8	59.0	21.9
Lead concentrate	830	1 46	59.0	4.4	22.6	3.5	0.5	22.2	0.3
Zinc concentrate	335	1.28	1.39	53.1	424.0	26.7	7.8	9.7	60.5
Tailing.....	27	0.24	0. 5	1.75	3680	18.6	12.9	9.1	17.3

## COPPER-ZINC ORES IN WHICH THE COPPER MINERAL IS NOT CHALCOPYRITE

As a working hypothesis it might be expected that the flotative behavior of ores in which chalcopyrite is not the copper mineral is similar to that of ores containing chalcopyrite as the only copper mineral. Yet this is not the case.

If chalcocite or bornite is present it is very difficult to keep the sphalerite or marmatite from becoming activated and from floating with the copper minerals. This effect must probably be ascribed to the rapid oxidation of chalcocite or bornite which takes place in aerated pulps and gives rise to a concentration of cupric ion sufficient to activate sphalerite even in solutions of high alkalinity.

In the treatment of chalcocite-sphalerite ores, the addition of a small amount of cyanide is of little avail as it partly wets the chalcocite at the same time as it partly deactivates the sphalerite. However, if considerable cyanide is added in strongly alkaline solution, so that the two minerals are first jointly inhibited even in the presence of such a strong collector as amyl xanthate, it is possible to make a separation when the cyanide has been consumed by reaction with chalcocite, the chalcocite floating slowly although sphalerite is still inhibited. The explanation is perhaps that reaction between cupric ion from the oxidizing chalcocite and the xanthate or other collecting ion takes place at the surface

TABLE 81.—METALLURGICAL RESULTS IN SELECTIVE FLOTATION OF BORNITE-SPHALERITE-GRANITE MIXTURE

Product	Weight, grams	Metal content		Recovery, per cent	
		Cu, per cent	Zn, per cent	Cu	Zn
Cleaner zinc concentrate..	42 0	6 55	55 3	12 0	83.0
Cleaner zinc tailing...	14 0	5 7	4 4	3 5	2.0
Cleaner copper concentrate.	12 5	46 8	19 5	26 0	8.5
Cleaner copper tailing	25 0	49 2	4 5	54 5	4.0
Rougher tailing.....	401	0 12	0.18	2.0	2.5

Zinc-copper selectivity index in roughing, 5.6.

Zinc-copper selectivity index in cleaning rougher zinc concentrate, 3.5.

Zinc-copper selectivity index in cleaning rougher copper concentrate, 2.2.

of the chalcocite before time is afforded for the cupric ion to activate the sphalerite.

The behavior of copper-zinc ores containing bornite and sphalerite but no chalcocite is not known. Since bornite oxidizes readily with the formation of a relatively insoluble film (tarnish)

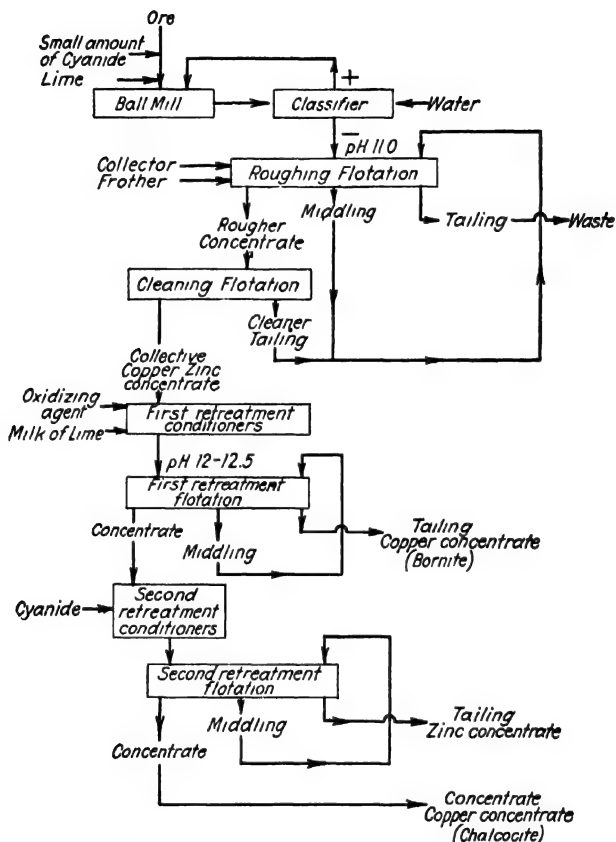


FIG. 71.—Proposed flotation flow-sheet for pyritic copper-zinc ore. It is assumed that the copper occurs as chalcocite and bornite.

at its surface, it may be expected that flotation of sphalerite (with a covellite filming) away from bornite can be accomplished in alkaline solution. This, indeed, is what happens with artificial mixtures of bornite and sphalerite, as may be seen from Table 81, which records metallurgical results obtained on a mixture of 420 g. granite, 40 g. sphalerite, and 40 g. bornite, ground together



and floated in a subaeration cell. The pulp was ground with lime, 2 lb. per ton, and chloride of lime, 2 lb. per ton, floated first with terpeneol, 0.02 lb. per ton, then with amyl xanthate, 0.03 lb. per ton. Each concentrate was cleaned with chloride of lime, 0.4 lb. per ton being used to retreat the first concentrate and 0.2 lb. per ton with lime, 0.6 lb. per ton, to retreat the second concentrate.

Laboratory results on a copper-zinc ore from Butte substantiated the findings concerning the relative floatability of sphalerite, bornite, and chalcocite. In the ore tested, the principal sulfide minerals were chalcocite, bornite, sphalerite, and pyrite. Microscope study showed that a marked tendency exists in alkaline circuits for chalcocite and sphalerite to float materially ahead of bornite if the circuit is sufficiently alkaline to inhibit pyrite. Advantage was taken of this to segregate a rougher copper-zinc concentrate containing chalcocite, bornite, and sphalerite into a chalcocite-sphalerite concentrate and a bornite tailing by raising the alkalinity under oxidizing conditions. Retreatment of the sphalerite-chalcocite concentrate with considerable cyanide allowed flotation of the chalcocite with inhibition of the sphalerite. Figure 71 shows schematically the flow-sheet suggested by this work.

### COPPER-LEAD ORES

The problem of separating lead-bearing from copper-bearing sulfides by flotation has been of little importance as compared to the problems of separating lead from zinc or copper from zinc. This is because lead and copper are rarely associated together in such proportion as to warrant the separation. It is shown below that there are definite limits between which the copper-lead ratio must lie in order to justify economically the separation. These limits are much narrower than in the case of the lead-zinc separation, partly because it is more difficult to separate copper-bearing from lead-bearing sulfides, but also because lead smelters penalize shippers for zinc but credit them for copper, even though at a lower rate than a copper smelter. Thus the margin of profit to be made by separating the copper sulfides from the lead sulfides is small. This consideration is supplemented by that of the distance to which the concentrate in smaller bulk would have to be shipped since smelters are not available everywhere.

Successive flotation of lead and copper from complex ores is a bit hazardous since copper is the more valuable of the two metals, and since flotation\* following activation of inhibited copper minerals may be less complete than flotation of copper minerals that have not been inhibited. Successive flotation of copper and lead appears remote as it is relatively more difficult to inhibit galena than the sulfides of copper. For the time being, at least, collective flotation of lead and copper from non-sulfide gangue, pyrite, and sphalerite should be considered as the logical first step, and selective retreatment of the collective concentrate as a subsequent operation.

**Economics of Segregation for Lead-bearing Copper Ores.—**

Few copper ores contain lead in sufficient amount for the latter to constitute a substantial fraction of the bulk of the copper concentrate (in which the lead would find its way in customary operations). However, as copper smelters do not pay for the lead contained in concentrates shipped to them, the lead contained in copper concentrates is a total loss to the shipper besides being a diluent for which freight and smelting charges have to be paid.

If a copper concentrate containing some lead were treated by selective flotation to separate the lead from the copper, a very high copper recovery in the copper product and a consequently low lead recovery in the lead product would be sought because of the disparity in the bulk of copper and lead present in the mixed product and because of the considerable shrinkage that would result in the value of the copper recovered in the lead concentrate. In view of the cost of retreating a collective concentrate, of the shrinkage in recovery of copper in the selective copper concentrate, and of the relatively small amount of lead concentrate that would be obtained, it is clear that the operation would be profitless unless the lead contents of the collective concentrate were above a certain substantial minimum.

To illustrate this proposition, let it be assumed that copper is worth 12 cts. a pound in a copper concentrate and 4 cts. in a lead concentrate, and that lead is worth 4 cts. a pound in a lead concentrate and nothing in a copper concentrate (this corresponds to a copper market near 16 cts. a pound and a lead market near 6.5 cts. a pound). For separations of lead from copper of the order of perfection that might be expected to obtain, analysis shows that the separation would be profitless unless the lead content of the

collective concentrate exceeded about one-fifth of the copper content of the same.

This may be illustrated further as follows: consider a collective copper-lead concentrate containing 25 per cent copper and variable amounts of lead from which a selective copper concentrate and a selective lead concentrate can be made. Assume further that 96 per cent of the copper in the collective concentrate goes to the copper product and that 60 per cent of the lead goes to the lead product. (Copper-lead selectivity index of 6.0.) The net returns from the segregated products would equal those from the mixed product for a lead content in the collective concentrate of  $3\frac{1}{3}$  per cent. The excess in the net returns from the segregated products over the returns from the collective concentrate would increase at the rate of approximately 50 cts. for each increase of one per cent of lead in the collective concentrate. If the collective concentrate contained 5 per cent lead, the crude profit per ton of collective concentrate creditable to the separation would be 80 cts. The cost of making the lead-copper separation is relatively high, because the feed to this flotation operation is a concentrated product containing a large sulfide surface to be affected by reagents, and therefore requires relatively large quantities of them, and because regrinding would probably be necessary. Putting the total retreatment cost at 80 cts. per ton of collective concentrate, a net profit on the retreatment of a mixed concentrate containing 25 per cent copper does not appear unless it contains 5 per cent lead or over (one-fifth the copper in the mixed concentrate or more).

In practice, unless a large-scale operation were involved, no attempt would be made to get an extra few cents per ton of mixed concentrate worth \$60 per ton unless success were certain. If a large-scale operation were involved, considerable investigation would be justified to disclose a way to make the copper-lead separation sufficiently fool-proof to justify retreatment of a collective lead-copper concentrate in which the lead-copper ratio is on the borderline. Unless the margin were 2 or 3 per cent of the value of the collective concentrate, the management of small enterprises would no doubt prefer to ship a mixed concentrate. In order for such a margin to appear from the retreatment of a collective concentrate, the lead content would have to be higher than one-fifth of the copper content in the collective concentrate. Indeed, for an indicated profit of 2.5

per cent on the value of the mixed concentrate, the lead content would have to be at least one-third of the copper content of the collective concentrate.

**Economics of Segregation for Copper-bearing Lead Ores.—**

The situation is different in what concerns lead ores. Lead ores frequently contain small quantities of copper whose recovery as a separate concentrate is more profitable than the segregation of small amounts of lead in a copper concentrate because of the greater value of copper than lead, and because of the nature of the usual smelter settlements for lead and copper products.

Considering smelter settlements for metals as above (copper worth 12 cts. per pound in a copper concentrate and 4 cts. in a lead concentrate; lead worth 4 cts. per pound in a lead concentrate and nothing in a copper concentrate), assuming a 50 per cent lead content in the collective concentrate and a copper-lead selectivity index of 6, as before (resulting from the recovery of 90 per cent of the lead in the lead concentrate and 80 per cent of the copper in the copper concentrate), the smelter returns from the assumed selective concentrates would equal or exceed the returns from a collective concentrate if the latter contained 3.1 per cent copper or over. If allowance of 80 cts. per ton of collective concentrate is made for the cost of concentrating, operations are breaking even for a collective concentrate containing  $3\frac{3}{4}$  per cent copper, and a profit of 3 per cent over the returns obtainable from the collective concentrate is shown if a collective concentrate containing 5 per cent copper is retreated.

This crude analysis indicates that the *segregation of copper and lead from a collective concentrate is economically justified only if the lead to copper ratio is between the limits of 10 and  $\frac{1}{3}$*  (for copper and lead markets as stated). It is likely that similar limits would appear if the analysis were made concerning the application of successive flotation of lead and copper. The results of the above analysis would be changed slightly through the use of actual rather than of open smelter schedules. Other changes would result from variations in metal prices, from the presence of other metals such as silver and zinc, and from variations in the distance to smelters, but the essence of the analysis is probably correct for most cases.

**Mineral Associations.**—In lead-copper ores the lead mineral is generally galena, but jamesonite has been recorded. Bournon-

ite, a lead-copper sulfide, occurs in some ores and cannot, of course, be segregated into concentrates of the two metals.

The commonest copper mineral is chalcopyrite, but tetrahedrite and tennantite are important because they frequently carry considerable silver. Chalcocite-galena and enargite-galena associations are also found.

#### SEPARATION OF CHALCOCITE FROM GALENA

Although associations of galena and chalcocite are not so frequent as those of galena and chalcopyrite, it is of interest to review the results of flotation tests on mixtures of these minerals.

Table 82 shows some results obtained on a synthetic ore composed of pure coarse galena, chalcocite, and granite ground for various lengths of time in a pebble mill and floated with a frother alone. Table 82 indicates that excellent separations

TABLE 82.—EFFECT OF FINENESS AND DURATION OF GRINDING ON SELECTIVE FLOTATION OF A SYNTHETIC LEAD-COPPER ORE COMPOSED OF GALENA, CHALCOCITE, AND GRANITE

Time of grind* in pebble mill, min.	Grade of concentrate		Recovery, per cent			Selectivity indices	
	Lead, per cent	Copper, per cent	Lead	Copper	Granite	Lead- copper	Lead- gangue
40	64.6	4.2	92.3	8.4	2.9	11.4	20.1
80	51.6	2.2	92.0	5.3	6.1	14.3	13.1
160	38.2	2.6	79.0	8.7	12.4	6.3	5.2
640	24.8	3.2	71.0	14.1	19.7	3.9	3.1

\* No reagents added for grinding. For flotation added terpineol 0.12 lb. per ton; pH, 7.8.

are obtainable by that means alone. The poor recovery of the chalcocite is perhaps to be traced to its high rate of oxidation, and the good recovery of galena to its relatively low rate of oxidation in the presence of oxygen-consuming chalcocite. The deleterious effect on the selectivity indices of overgrinding is well shown.

Figure 72 shows some results obtained on a similar synthetic ore at various pH values (using HCl or NaOH to vary pH). Optimum results are apparently obtained in the pH range of 8.5 to 10.

Table 83 shows the effect of small additions of a strong collector on the copper-lead selectivity index. It is entirely clear that the xanthate increases both the lead and the copper recovery, but that since most of the lead is recoverable without collector, the effect of that reagent in the main is to increase the copper recovery, thereby affecting adversely the lead-copper selection.

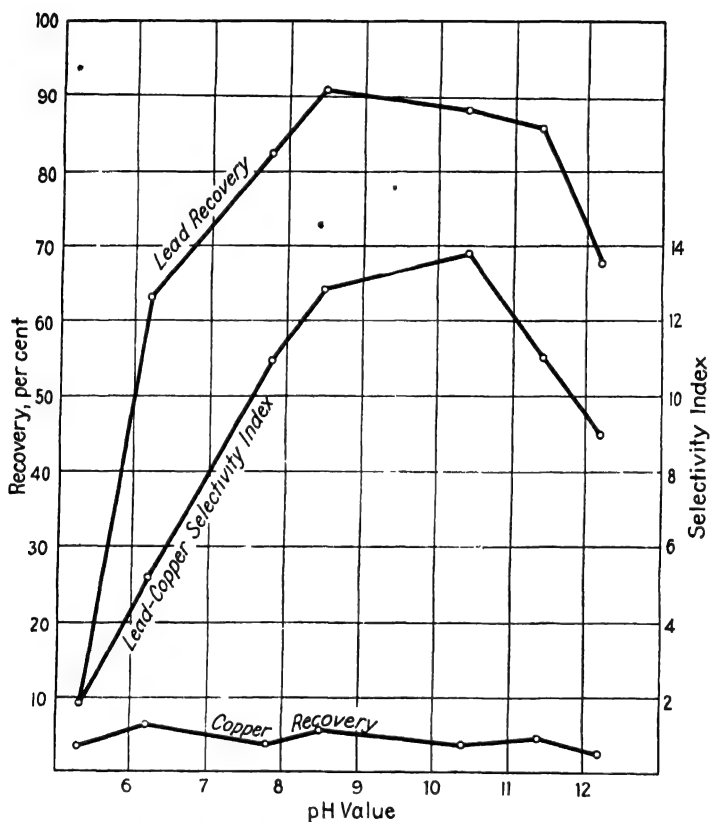


FIG. 72.—Separation of galena from chalcocite.  
Effect of pH on mixtures of galena, chalcocite and granite, using terpineol (0.12 lb. per ton) as the only reagent.

Table 84 presents results obtained with deslimed, relatively pure chalcocite mixed with galena having slightly oxidized surfaces. The results indicate the possibility of separating these minerals by floating one mineral or the other, as the case may be, depending upon the reagents added in the flotation cell.

TABLE 83.—EFFECT OF A STRONG COLLECTOR (AMYL XANTHATE) ON LEAD-COPPER SEPARATION FROM MIXTURES OF CHALCOCITE, GALENA, AND GRANITE (30-90-380)

Product	Xanthate added, lb. per ton				
	0	0.005	0.01	0.02	0.05
pH of tailing pulp.....	9.2	9.2	9.4	9.0	9.2
Lead content of concentrate, per cent. .	39.1	32.7	30.6	30.2	20.5
Copper content of concentrate, per cent .	9.2	17.4	23.3	25.6	40.0
Lead content of tailing, per cent. .	1.6	1.4	1.35	1.05	0.85
Copper content of tailing, per cent	12.7	11.0	10.7	9.6	5.6
Lead-copper selectivity index ..	5.8	3.8	3.2	3.3	1.8

TABLE 84.—EFFECT OF INHIBITING AGENTS ON CHALCOCITE-GALENA SEPARATION

Metallurgical data	Test 1	Test 2	Test 3	Test 4	Test 5
Reagent					
Terpineol . . . . .	0.10	0.10	0.10	0.10	0.20
Ethyl xanthate. . . . .	0.10	0.12	0.12	0.10	
Amyl xanthate. . . . .					0.025
Sodium carbonate . . . .			2.0	2.0	4.0
Potassium chromate		0.50	0.50		6.0
Potassium ferrieyanide				2.0	
Lead nitrate . . . . .			0.80		
Recoveries					
Galena in concentrate..	51	8	23	47	24
Chalcocite in concentrate	68	86	98	5	84
Selectivity index in favor of copper	1.5	8.4	12.8		4.1
Selectivity index in favor of lead				4.1	

## SEPARATION OF CHALCOPYRITE FROM GALENA

The separation of galena from chalcopyrite is relatively easier than that of galena from chalcocite, as chalcopyrite is readily inhibited by cyanide if the latter is used in sufficient amount. Through the use of cyanide, therefore, it is possible to separate galena from chalcopyrite rather well. A separation in the opposite direction (by sinking galena) can be made in acid circuits using a copper salt and a dichromate. However, the separation appears more difficult in that way.

Experiment shows that satisfactory separation of galena from chalcopyrite requires the presence of a small but definite free cyanide-ion concentration in the solution. As contact proceeds between the solution and the ore, the free cyanide concentration

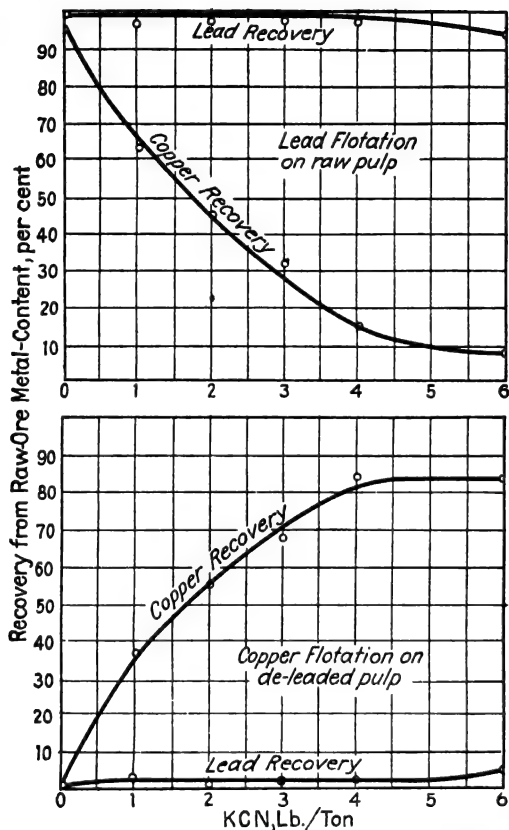


FIG. 73.--Separation of galena from chalcopyrite.

Effect of additions of potassium cyanide on mixtures of galena, chalcopyrite and granite. Reagents to float galena were terpineol, 0.10 lb. per ton, and potassium amyl xanthate, 0.01 lb. per ton; to float chalcopyrite, copper sulfate, 1.0 lb. per ton, terpineol, 0.05 lb. per ton, and amyl xanthate, 0.05 lb. per ton.

decreases to the vanishing point. The quantity of cyanide yielding best results is one large enough to prevent extremely rapid disappearance of free cyanide, as well as small enough not to provide too large an excess of that ion.

Figure 73 shows the results obtained by successive flotation on a synthetic mixture of chalcopyrite, galena, and granite, ground together with cyanide and floated under different conditions.



Table 85 shows the influence of particle size. The lead-copper separation is clearly poorer the finer the particle size.

TABLE 85.—INFLUENCE OF PARTICLE SIZE ON METALLURGICAL RESULTS OBTAINED IN FLOTATION OF A CHALCOPYRITE-GALENA-GRANITE MIXTURE

Particle size, mesh	Lead concentrate		Copper concentrate		Tailing		Lead-copper selectivity index in lead cycle
	Pb, per cent	Cu, per cent	Pb, per cent	Cu, per cent	Pb, per cent	Cu, per cent	
150/200	83.6	0.03	0.08	32.5	0.015	0.026	544
200/280	83.2	0.29	0.12	32.6	0.020	0.069	174
280/400	83.6	1.14	0.17	32.0	0.020	0.128	88
400/800	71.0	5.15	0.31	31.1	0.026	0.285	30
—800	59.2	5.9	5.6	25.5	0.031	0.584	7.3

An interesting practical illustration is furnished by the following example. From a copper concentrate containing 24.0 per cent copper (as chalcopyrite), 10.5 per cent zinc, and 6.0 per cent lead it was found possible to make (by a roughing-cleaning operation involving no regrinding) three products of widely different composition (Table 86).

TABLE 86.—SEGREGATION OF A LEAD-BEARING COPPER CONCENTRATE INTO A LEAD PRODUCT AND A COPPER PRODUCT

Product	Pb, per cent	Zn, per cent	Cu, per cent	Fe, per cent	Insoluble, per cent
Concentrate.....	35.3	12.5	12.3	11.2	0.5
Middling.....	13.2	11.2	21.7	20.5	1.0
Tailing.....	0.9	7.7	26.5	26.1	1.2

Of these products the tailing only would be commercially satisfactory. The results, however, are promising. The reagents employed were cyanide, lime, and zinc sulfate.

**Utah-Apex Mill.**—Separation of chalcopyrite from galena has been effected on a commercial scale at the mill of the Utah-Apex Mining Company, Bingham, Utah, during 1927 to 1929 but it has recently been suspended. The results obtained were satisfactory, the suspension in the operation having been caused by scarcity of ore rather than by unsatisfactory metallurgical results.

The flotation division of the flow-sheet at the copper-lead plant of the Utah-Apex is as follows (Fig. 74): the classifiers overflow to a rougher MacIntosh cell<sup>1</sup> which collects the copper and lead as a combined concentrate. This concentrate is not truly a collective concentrate since the iron and zinc are not collected in it (due to the addition in the grinding mill of iron- and zinc-

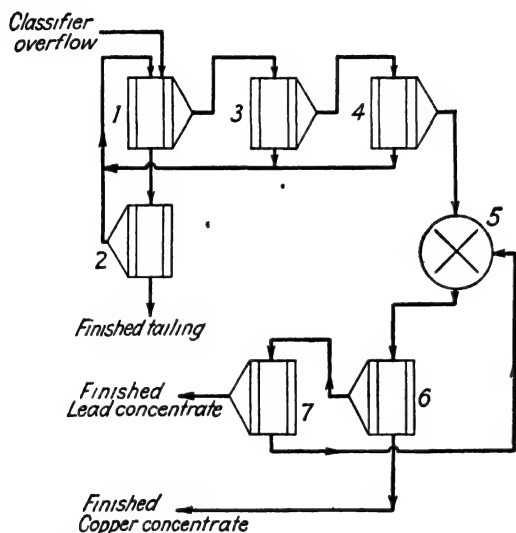


FIG. 74.--Flotation division, Utah-Apex mill (copper-lead ore).

inhibiting reagents), but for convenience it may be termed the rougher collective concentrate. The tailing from ① goes to a scavenging cell ② from which a finished tailing and a middling are made. The finished tailing contains considerable pyrite and some sphalerite. So far, it has not been economical to recover the zinc, but this may be done if a higher market for that metal prevails. The middling from ② is returned to ① and the concentrate from ① is cleaned twice ③, ④ in MacIntosh machines, the cleaner and recleaner tailings being returned to the primary rougher for further treatment.

The recleaned concentrate from ④ is the cleaned collective concentrate which is ready for further treatment. It is conditioned for about 30 min. in surge tank ⑤ then segregated into a copper-lead middling and a finished copper product by the first retreatment MacIntosh cell ⑥. The froth from ⑥ is refloats in the second retreatment cell ⑦ yielding a finished lead

concentrate and a lead-copper middling which is returned to the conditioning tank (5).

Typical metallurgical results obtained at the Utah-Apex lead-copper section are presented in Table 87 and the reagents in Table 88. It should be noted that the amount of cyanide added

TABLE 87.—METALLURGICAL RESULTS IN LEAD-COPPER SECTION AT UTAH-APEX MILL (1928)

Product	Metal content			Recoveries, per cent	
	Pb, per cent	Cu, per cent	Fe, per cent	Pb	Cu
Feed. ....	7 0	1 8	15		
Lead concentrate ....	50	5	10	88.7	34.5
Copper concentrate.....	6	22	35	3.6	49.3
Tailing .....	0.65	0 35	.....	7.7	16 1

Lead-copper selectivity index in retreatment section, 6.0.

TABLE 88.—REAGENTS IN LEAD-COPPER SECTION AT UTAH-APEX MILL (1928)

Added to	Reagent	Quantity, lb. per ton
Ball mill. ....	Sodium carbonate	2.0
	Sodium cyanide	0 15
	Thiocarbamilid	0.09
Collective cells	Ethyl xanthate	0 10
	Pine oil	0 08
	Aerofloat (dithiophosphoric acid)	0.15
Retreatment conditioner (pH 9.5).....	Sodium carbonate	1 25
	Sodium cyanide	0 5

in the primary flotation circuit must be carefully limited in order not to result in undue copper losses in the tailing.

#### SEPARATION OF ENARGITE FROM GALENA

Separation of enargite from galena is not so easy as that of chalcocite or chalcopyrite from galena. Broadly speaking, two methods are available: (1) dissolution of part or all of a surface layer of enargite in cyanide solution, resulting in inhibition of the copper mineral; (2) coating of galena with an insoluble chromate

The flotation division of the flow-sheet at the copper-lead plant of the Utah-Apex is as follows (Fig. 74): the classifiers overflow to a rougher MacIntosh cell<sup>1</sup> which collects the copper and lead as a combined concentrate. This concentrate is not truly a collective concentrate since the iron and zinc are not collected in it (due to the addition in the grinding mill of iron- and zinc-

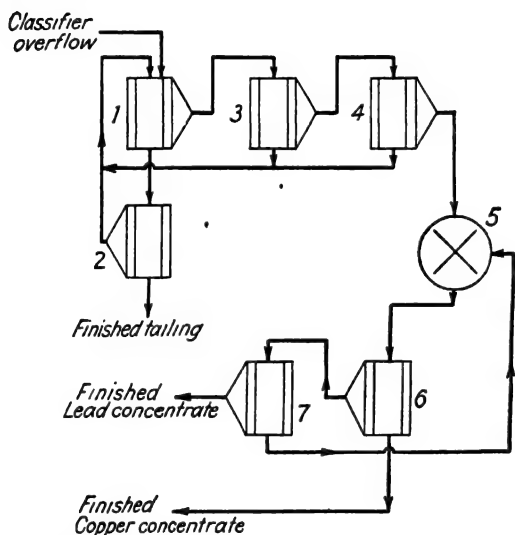


FIG. 74.—Flotation division, Utah-Apex mill (copper-lead ore).

inhibiting reagents), but for convenience it may be termed the rougher collective concentrate. The tailing from ① goes to a scavenging cell ② from which a finished tailing and a middling are made. The finished tailing contains considerable pyrite and some sphalerite. So far, it has not been economical to recover the zinc, but this may be done if a higher market for that metal prevails. The middling from ② is returned to ① and the concentrate from ① is cleaned twice ③, ④ in MacIntosh machines, the cleaner and releaner tailings being returned to the primary rougher for further treatment.

The releaned concentrate from ④ is the cleaned collective concentrate which is ready for further treatment. It is conditioned for about 30 min. in surge tank ⑤ then segregated into a copper-lead middling and a finished copper product by the first retreatment MacIntosh cell ⑥. The froth from ⑥ is refloated in the second retreatment cell ⑦ yielding a finished lead

concentrate and a lead-copper middling which is returned to the conditioning tank ⑤.

Typical metallurgical results obtained at the Utah-Apex lead-copper section are presented in Table 87 and the reagents in Table 88. It should be noted that the amount of cyanide added

TABLE 87.—METALLURGICAL RESULTS IN LEAD-COPPER SECTION AT UTAH-APEX MILL (1928)

Product	Metal content			Recoveries, per cent	
	Pb, per cent	Cu, per cent	Fe, per cent	Pb	Cu
Feed. . . . .	7 0	1 8	15		
Lead concentrate . . . . .	50	5	10	88 7	34.5
Copper concentrate.....	6	22	35	3.6	49.3
Tailing . . . . .	0.65	0 35	.....	7.7	16.1

Lead-copper selectivity index in retreatment section, 6.0.

TABLE 88.—REAGENTS IN LEAD-COPPER SECTION AT UTAH-APEX MILL (1928)

Added to	Reagent	Quantity, lb. per ton
Ball mill. . . . .	{ Sodium carbonate	2.0
	{ Sodium cyanide	0 15
	{ Thiocarbamilid	0.09
	{ Ethyl xanthate	0 10
Collective cells.	{ Pine oil	0.08
	{ Aerofloat (dithiophosphoric acid)	0 15
Retreatment conditioner (pH 9.5).....	{ Sodium carbonate	1.25
	{ Sodium cyanide	0 5

in the primary flotation circuit must be carefully limited in order not to result in undue copper losses in the tailing.

#### SEPARATION OF ENARGITE FROM GALENA

Separation of enargite from galena is not so easy as that of chalcocite or chalcopyrite from galena. Broadly speaking, two methods are available: (1) dissolution of part or all of a surface layer of enargite in cyanide solution, resulting in inhibition of the copper mineral; (2) coating of galena with an insoluble chromate

by treatment in an oxidizing acid circuit in which the dichromate ion is present. This results in inhibition of the lead mineral.

Some results are shown in Table 89.

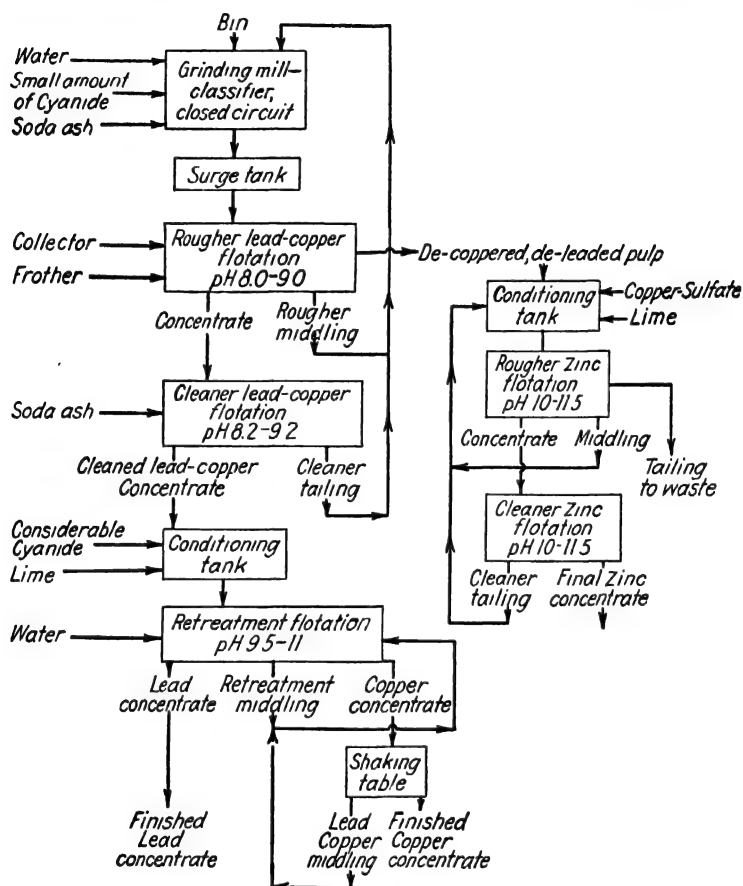


FIG. 75.—Proposed flotation flow-sheet for a copper-lead-zinc ore.

It is assumed that the ore consists of chalcopyrite, galena, sphalerite (or marmatite), and pyrite (or pyrrhotite) in a silicate gangue.

**Copper-lead-zinc Ore.**—Figure 75 shows a proposed selective flotation flow-sheet for the treatment of a copper-lead-zinc ore consisting of chalcopyrite, galena, marmatite, and pyrite (or pyrrhotite) in a silicate gangue. This flow-sheet features essentially the following:

1. Successive flotation of a collective lead-copper concentrate and of a selective zinc concentrate.

2. Retreatment of the collective lead-copper concentrate for lead flotation and copper inhibition.
3. Use of a suitable number of cleaning steps.
4. Use of regrinding, if necessary.
5. pH control.
6. Reaction-time control in conditioning tanks.

TABLE 89.—SEPARATION OF GALENA FROM ENARGITE IN SYNTHETIC GALENA-ENARGITE-GRANITE MIXTURES (50-50-400)

Sodium cyanide, lb. per ton	Recovery, per cent, in				Lead-copper selectivity index in first float
	First concentrate*		Second concentrate†		
	Pb	Cu	Pb	Cu	
0.5	85	62	5	21	1.9
1.0	89	22	..	..	5.3
2.0	98	13	1	86	18.1
3.0	97	6	2	93	22.5
4.0	96‡	11	3	2§	14.0

\* Using terpeneol, 0.10 lb. per ton; amyl xanthate, 0.02 lb. per ton.

† Using terpeneol, 0.075 lb. per ton; amyl xanthate, 0.05 lb. per ton; copper sulfate, 1.0 lb. per ton.

‡ Lead floated slowly

§ Copper sulfate (1.0 lb. per ton) was insufficient to overcome the effect of the residual cyanide.

### COPPER-NICKEL ORES

In its commonest and most abundant form, nickel occurs as a sulfide associated with chalcopyrite and with iron sulfides, particularly pyrrhotite. The separation of copper and nickel sulfides from the pyrrhotite and silicates with which they are usually associated would indeed be a useful application of flotation, as the tonnage of copper-nickel material to be smelted for a given tonnage of the metals to be produced would be much reduced. Although some progress has been made toward the production of selective concentrates from the usual copper-nickel ores, the problem is hardly solved.

Separation of chalcopyrite from pyrrhotite, pyrite, and arsenopyrite, which are the three principal iron sulfides barren of copper and nickel, is readily accomplished as described in Chap. VIII. But separation between the nickeliferous sulfides and pyrrhotite is not satisfactory, the nickel recovery in particular

being poor if pyrrhotite rejection is good. This is perhaps to be ascribed to ignorance of the structural association of the nickel and iron, and to the possibility that some nickel occurs in solid solution in the pyrrhotite.

Nickel occurs generally as pentlandite (an iron-nickel sulfide), millerite (nickel sulfide), gersdorffite (a nickel arsenide), and in other rarer forms.

The nickel deposits of the Sudbury basin, Ontario, contain gold and precious metals of the platinum group. The particular occurrence and association of these metals are not exactly known.

Laboratory experiments indicate that the susceptibility to lime circuits increases from chalcopyrite, through the nickel minerals, to pyrrhotite, so that by pH control flotation in the order copper, nickel, iron, is possible. Although distinct selection between nickel and iron can be obtained, the nickel content of the denickeled pulp is too high to be acceptable. In some experiments with an ore from the Falconbridge mine, the copper-nickel and copper: free-iron selectivity indices in the copper circuit were about 6 and 20, and the nickel-iron index in the nickel-floating cycle about 6.

**Copper Cliff Concentrator**<sup>(4)</sup>.—The Copper Cliff concentrator of the International Nickel Company located near Sudbury, Ontario, treats daily by part-selective flotation up to 8000 tons of copper-nickel ore.

Treatment involves the following essential steps:

1. Selective flotation of part of the chalcopyrite.
2. Cleaning of the rougher chalcopyrite froth.
3. Collective flotation of the remainder of the sulfides.
4. Cleaning of the collective nickeliferous froth.

The flow-sheet of one section in the flotation division is shown in Fig. 76. The ore pulp in each section (16 sections in the mill) goes through two 20-ft. by 30-in. MacIntosh copper roughers in series ①, ②, then through two 20-ft. by 30-in. MacIntosh copper-nickel roughers in series ⑧, ⑨. The tailing from the 16 sections is floated further in six similar machines used as scavengers in parallel ⑩.

The rougher copper concentrate of each section is cleaned in one 12-ft. by 36-in. MacIntosh cleaner ③, and recleaned in a similar machine ④. The recleaned concentrate from all the sections is classified into sand and slime by two 8-in. by 18-ft. Dorr Duplex classifiers ⑤; the slime is thickened in two 55-ft.



tray thickeners ⑥; and the thickened slime together with the sand is filtered in two Dorrco filters.

The rougher and the scavenger dicker concentrates and the copper-cleaner tailing of each section are joined and cleaned together in two 12-ft. by 36-in. MacIntosh cleaners in series ⑪, ⑫. The tailing from ⑫ is returned to the head of ⑧. The

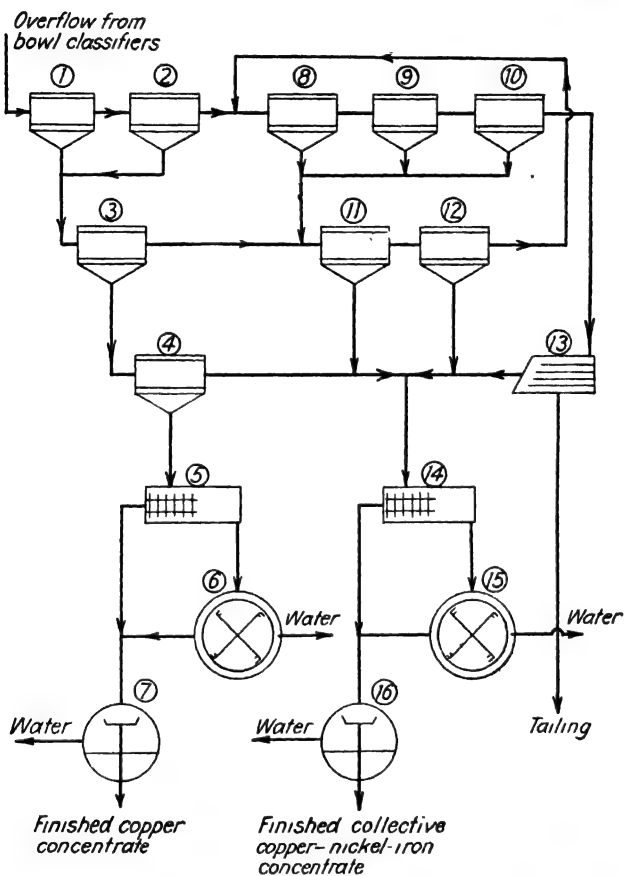


FIG. 76.—Flotation division, Copper Cliff concentrator.

concentrate from ⑪ and ⑫, the copper recleaner tailing from ④ and a table ⑬ concentrate obtained from the final flotation tailing before discarding, are joined and thickened and filtered together in a plant similar to that used in dewatering the copper concentrate, but of double the capacity ⑭, ⑮, ⑯. The dewatered concentrate is the finished copper-nickel concentrate.

The reagents used are presented in Table 90.

TABLE 90.—REAGENT CONSUMPTION AT COPPER CLIFF  
(After MacDonald.)

Reagent	Lb. per ton	Added to
No. 80 Pensacola flotation oil	0.17	Copper roughers and nickel roughers
No. 15 aerofloat. . . . .	0.06	Nickel roughers
No. 25 aerofloat. . . . .	0.06	
Pine oil (No. 5, G.N.S.) . . . .	0.30	Copper roughers
Sodium xanthate. . . . .	0.22	Nickel roughers
Copper sulfate . . . . .	0.40	Nickel roughers
Lime. . . . .	1.60	Ball mill

Careful alkalinity control by the colorimetric method is practiced. Table 91 presents typical pH values of the pulp at various points in the circuit.

TABLE 91.—pH OF MILL SOLUTIONS AT COPPER CLIFF  
(After MacDonald.)

	pH
Fresh water supply (Kelley Lake)..	6.8
Thickener overflow . . . . .	8.0
Wash water in flotation cell launders. . . . .	6.7
Bowl classifier overflow (feed to copper cells).	8.2
Feed to copper-nickel cells . . . . .	7.6
Final tailing. . . . .	7.4
Copper cleaner feed. . . . .	8.6
Copper recleaner feed. . . . .	8.8
Tailing pond. . . . .	6.1



## CHAPTER XI

### OXIDIZED ORES OF COPPER, LEAD, AND ZINC

The occurrence of oxidized ores is more erratic and on a smaller scale than that of sulfide ores. Oxidized ores are mineralogically more complex but easier to smelt or leach than sulfide ores. As a result, the field of application of flotation is smaller.

Many attempts have been made to float oxidized ores, but the results have been disappointing. At first technical as well as economic results were lacking. The technical difficulties have been surmounted in the case of most oxidized lead ores and of some copper ores, but the economic aspects of the solution to the problems are not entirely satisfactory.

Oxidized copper ores are generally free of lead or zinc minerals. Their concentration involves, therefore, no separation from these metals. Oxidized lead ores occasionally contain zinc, sometimes copper, and frequently considerable silver. Oxidized zinc ores have received relatively little attention because sulfide zinc ores are plentiful and because the demand for zinc in recent years has been insufficient to make the concentration of oxidized ores economically attractive.

As contrasted with the selective application of flotation to sulfide ores, the application to oxidized ores is essentially collective, at least in its present stage of development. Future developments will possibly place more emphasis on segregation of the valuable metals from each other, but the immediate goal is to get good recoveries of gold, silver, copper, and lead, with fair rejections of silica and lime.

**Oxidized Minerals of Copper, Lead, and Zinc.**—The minerals of copper which are collectively grouped as oxidized include the two basic carbonates, *azurite* and *malachite*; the two oxides, *cuprite* and *melanconite*; and various silicates of which *chrysocolla* is typical. Of these minerals, malachite and chrysocolla are the commonest both in respect to quantity and to frequency of occurrence.

The principal oxidized lead minerals are *cerussite*, the carbonate; *anglesite*, the sulfate; *plumbojarosite*, a basic sulfate of lead

and iron; *wulfenite*, the molybdate; *mimetite*, the arsenate; and *pyromorphite*, the phosphate. The chromate is also known.

The principal oxidized zinc minerals are *smithsonite*, the carbonate; and *calamine*, the silicate.

**Occurrence of Precious Metals.**—The occurrence of silver is difficult to determine directly on account of the relatively minute quantities of the metal which when present make an ore. The form in which silver occurs in oxidized ores is therefore largely a matter of speculation more or less supported by circumstantial evidence. Hahn<sup>(9)</sup> found that in the Tintic District of Utah silver in oxidized form occurs in association with oxidized lead minerals, in association with iron oxide, in association with oxidized lead minerals, in association with iron oxide, in association with quartz, and as a jarosite.

Besides the occurrences noted by Hahn, oxidized silver minerals involve several halides, sulfates, phosphates, arsenates, and carbonates. The chloride and bromide are particularly likely to occur as smears on fracture walls in the oxidized zone of fissure veins.

The occurrence of gold is still less certain. Some of the gold may be occluded in remnants of unoxidized sulfides, particularly pyrite, but most of it probably occurs as native gold, in various stages of dissemination, and more or less occluded in, and surrounded by, colloidal iron oxides.

**Gangue in Oxidized Ores.**—In considering the treatment of oxidized ores it is most important to pay attention to the chemical composition and structure of the gangue as well as to the size of the particles to which it breaks.

There are two principal varieties of gangue: the siliceous and the carbonate types in which the most abundant constituents are silica and calcium carbonate, respectively. Variations from these two principal types result if iron oxides or alumina are present.

Iron oxide results from the decomposition of iron-bearing sulfides, particularly pyrite; structurally, this limonitic material is composed of cemented colloidal grains which on grinding give rise to extremely fine particles. These particles, if present in sufficient quantity, smear over every kind of particle, so that flotation may be defeated even if limonite-dispersing conditions prevail. Iron oxides are definite consumers of reagents, particularly of sulfide ion. Because of their fine size, limonite

particles have a greater tendency to report in the concentrate than silica or calcareous particles.

Clayey (aluminous) material is also harmful but it rarely occurs in as large quantity as limonite.

Colloidal silica has been reported to occlude precious metals and to obscure the surface of minerals to be floated.

From all standpoints a brittle siliceous gangue with small quantities of limonitic and clayey materials is the most desirable; a carbonate gangue comes next, and with increasing amounts of limonite and of clayey minerals successful concentration by flotation becomes increasingly expensive and difficult.

### LEAD-SILVER ORES

To date oxidized lead-silver ores are the only oxidized ores to which extensive application of flotation has been made.

It occurred to Schwarz<sup>(16)</sup> that if oxidized ores were sulfidized through interaction with a soluble sulfide, the ore might subsequently be floated with the usual reagents adapted to sulfide flotation. Until recently this idea has been the basis of substantially all the industrial applications of flotation to oxidized lead-silver ores<sup>(16a)</sup>.

If the gangue is not a carbonate, oxidized lead minerals can be collected selectively through the use of soaps at the proper pH.

If used in large amount in the absence of a sulfidizing treatment, organic sulfhydrates having a relatively long hydrocarbon chain collect oxidized lead minerals regardless of the character of the gangue. This method, although not economical because of the high consumption of collector, has given the most positive separation between the oxidized base-metal minerals and associated gangue.

**Sulfidizing.**—The reaction between a soluble sulfide and certain oxidized lead minerals is very rapid; in fact it can be used to guide table concentration. This is done by allowing some alkali sulfide solution to fall on the table while in operation: the immediately acquired brown or black color of the sulfide coating on the oxidized lead minerals allows an estimation of the otherwise invisible demarkation between concentrate and tailing.

All lead minerals do not react as readily with a soluble sulfide as lead carbonate with which the reaction is most rapid (Fig. 7,

Chap. V); with anglesite the reaction is positive but slower; with the phosphate, chromate, molybdate, and arsenate the reaction is unsatisfactory.

Although the nature of the sulfidizing reaction has not been thoroughly investigated, it is certain that differences between the sulfidized crust and galena must exist. In appearance the sulfidized coating is rather dull, resembling sooty chalcocite rather than galena, unless it is formed on cerussite having well-defined crystal faces. The coating is also irregular in thickness as witnessed by the range in color of the coating from spot to spot. From these observations it may be inferred that the coating is microcrystalline and discontinuous. From the relative specific gravities of lead sulfide and lead carbonate it must be concluded that each crystal unit of cerussite is replaced by a crystal unit of lead sulfide plus a void. Accordingly the coating is either amorphous, or else accretion of several crystal units of lead sulfide to microcrystalline galena must have taken place, resulting in the formation of pores large enough to permit access of dissolved substances, particularly oxidizing agents. Viewed from the standpoint of catalysis, the lead sulfide coating resulting from a sulfidizing treatment on the surface of oxidized lead minerals is in an eminently reactive state. It may therefore be considered, temporarily at least, that sulfidized crusts on oxidized lead minerals differ from galena by their microcrystalline, discontinuous, and much more oxidizable character.

Although substantially unoxidized galena is floated easily with a frother alone, poor results are obtained in treating similarly a cerussite pulp previously sulfidized thoroughly and washed. This is perhaps ascribable to the oxidizability of the coating or to its discontinuous character.

Sulfidized lead minerals resemble galena in that they are collected by sulfhydryde collectors. In the case of galena it has been inferred<sup>(17)</sup> that oxidation patches at the surface react with organic sulfhydryde ions by metathesis, forming a coating of the lead salt of the organic sulfhydryde. The same thing must occur in the case of sulfidized lead minerals which begin to reoxidize as soon as the sulfide-ion concentration reaches the vanishing point. In the case of oxidized minerals that have been sulfidized there may well be simultaneous direct reaction between the unsulfidized portions of the mineral and the collecting agent.

**Sulfidizing Agents.**—Sulfidizing agents that have been recommended for the treatment of oxidized lead ores include sodium, potassium, and ammonium sulfides, barium and calcium polysulfides, and hydrogen sulfide. Alkali sulfides and hydrogen sulfide are obtainable in a relatively pure state. On the other hand, calcium and barium polysulfides, which are made by the reaction of a lime or baryta water-slurry with flowers of sulfur at boiling temperature, are generally indefinite mixtures of complex sulfur compounds known as polysulfides to indicate that they contain relatively more sulfur than plain sulfides.

All sulfidizing agents except hydrogen sulfide are at the same time alkaline, so that the use of a quantity sufficient to sulfidize all of the mineral may result in an overalkaline pulp, necessitating the use of sulfuric acid as a corrective.

Sulfur, sulfurized oils, and colloidal sulfur have been recommended as sulfidizing agents, but it is reasonably certain that they are relatively ineffective as such. Sulfurized oils, also known as "reconstructed" oils, were first devised for the treatment of oxidized ores but their use was later extended to the treatment of sulfide ores. In some sulfurized oils the sulfur has become associated with the constituents of the oil to form new molecular species containing the sulfur atom and capable of reaction with mineral surfaces much in the same way as the xanthates. Sulfurized oils are therefore not so much sulfidizing as collecting agents.

Table 92 shows the results obtained on floating crystalline cerussite with amyl xanthate after sulfidizing with sodium sulfide,

TABLE 92.—EFFECT OF SULFIDIZING ON FLOTATION OF PURE CERUSSITE (100/800 MESH)

Reagents, lb. per ton			Recovery, per cent,	Color of froth
Terpincol	Amyl xanthate	Sodium sulfide		
0.15	....	.....	13	White
0.15	0.10	....	52	Pale cream
0.15	0.10	0.20	94	Very pale brown*
0.15	0.10	0.40	96	Pale brown*
0.15	0.10	1.00	98	Brown*
0.15	0.04	1.00	96	Brown

\* Froth appeared as though too much collector had been used



and compares these results with those obtained on the same mixture without sulfidizing. It is apparent that if the cerussite is sulfidized the collector requirement is reduced.

**Collection with Fatty Acids and Soaps.**—The flotation of cerussite and anglesite with soaps is a very easy matter, but their



FIG. 77.—Crystalline cerussite coated with lead thiocresylate,  $\times 12$ . p-thiocresol concentration ca. 0.025 per cent; methyl alcohol, concentration ca. 5.0 per cent. Reaction time, 10 minutes. The specimen was half-coated with paraffin (light), immersed in the thiocresol solution and photographed in the solution. The gas bubbles (possibly  $\text{CO}_2$ ) adhering to the thiocresylate grew slowly during the reaction.

separation from gangue is difficult. So far it has been found impossible to separate cerussite or anglesite from the carbonates of the alkaline earths, manganese, or iron through the use of fatty acids or soaps. Non-selective flotation of all the carbonates takes place even though the various carbonates require different amounts of the collector to give equivalent recovery when they are floated individually<sup>(6)</sup>.

TABLE 93.—CONCENTRATION OF OXIDIZED LEAD ORE BY MEANS OF INTERMEDIATE SATURATED FATTY ACIDS

Reagent	Reagent amount, lb. per ton	Grade of concentrate, per cent Pb	Lead recovery, per cent	Selectivity index, lead to gangue
Pelargonic acid. . . . .	3.0	34.9	81	5.4
Heptylic acid. . . . .	5.0	29.3	69	2.8

The separation of oxidized lead minerals from siliceous gangue can be accomplished with fatty acids. In Table 93 are presented some results obtained with pelargonic and heptylic acids on a Utah ore containing 10.8 per cent lead.

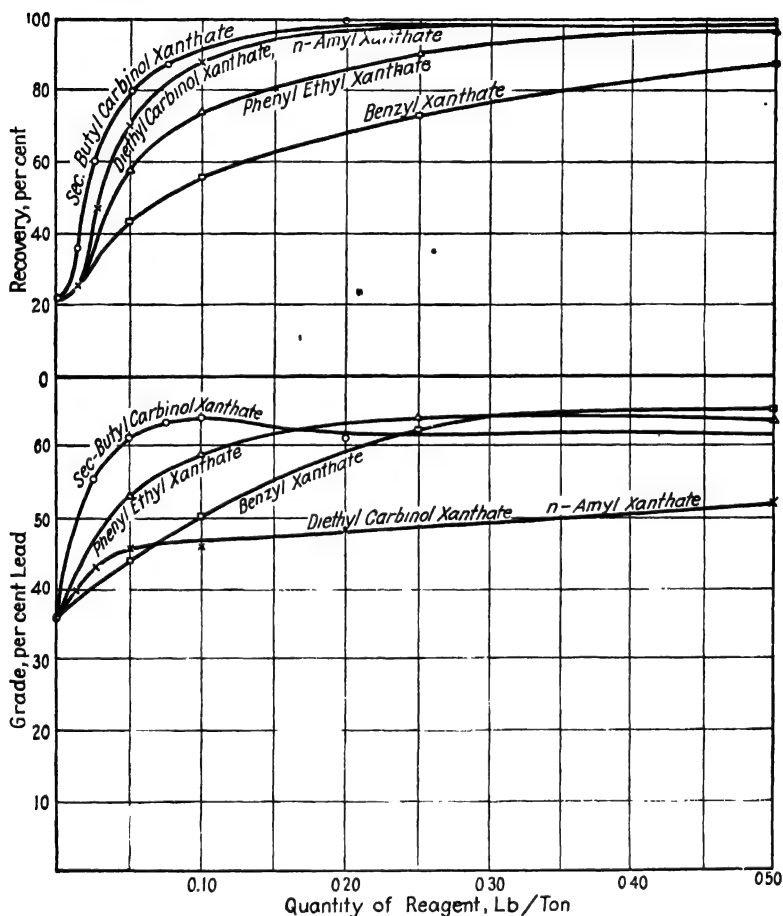


FIG. 78.—Cerussite-calcite separation.

1:4 mixture of 100/600-mesh cerussite-calcite mixtures was separated using terpineol, 0.20 lb. per ton, and potassium xanthates as shown. Pre-agitation, 45 seconds; flotation, 4 minutes; pH range, 8.2–8.8; temperature 21 to 22°C.

**Collection with Organic Sulfhydrates.**—The effect of treating lead carbonate with a xanthate, mercaptan, or thiophenol is to form at the surface of the mineral a crust of lead xanthate, mercaptide, or thiophenate. This is readily observed with

thiocresol whose lead salt is sufficiently dark colored for the phenomenon to be obvious to the naked eye (Fig. 77).

In the flotation of cerussite from a carbonate gangue or from quartz the effect of collectors whose molecules contain homo-

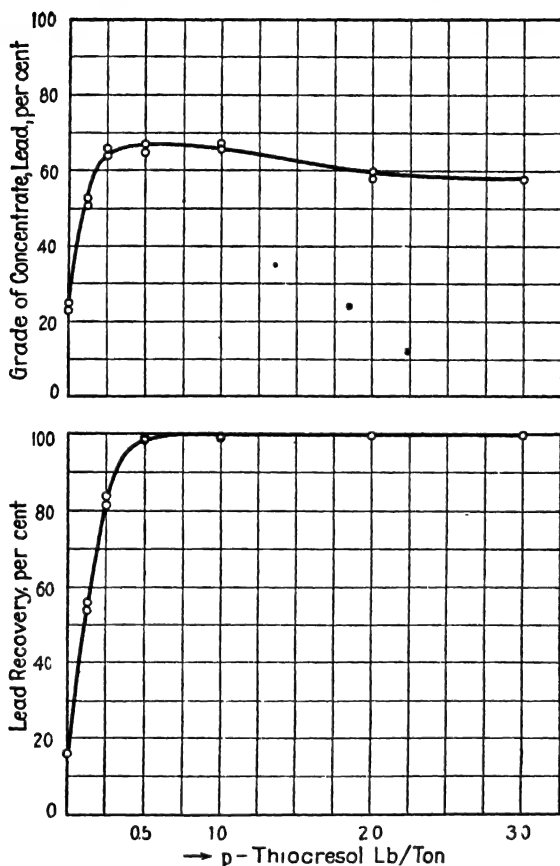


FIG. 79.—Cerussite-calcite separation. (After Anderson.)

1:4 mixture of 100/600-mesh particles was separated using p-thiocresol, as shown, together with terpeneol, 0.20 lb. per ton. Pre-agitation, 2 minutes; flotation, 6 minutes; pH range, 8.0-8.2; temperature 18 to 21°C.

gous aliphatic hydrocarbon radicals is much the same qualitatively, but the quantitative effect is highest for the amyl compounds; then for the compounds immediately higher in the homologous series, that is the hexyl, heptyl, and octyl compounds; then, in turn, for the butyl, propyl, ethyl, and methyl compounds. Methyl xanthate is almost impotent to float cerussite; but amyl

xanthate is so effective that 0.10 lb. per ton is sufficient to give an excellent recovery of the lead mineral from a deslimed artificial ore containing one-fifth cerussite and four-fifths calcite (Fig. 78).

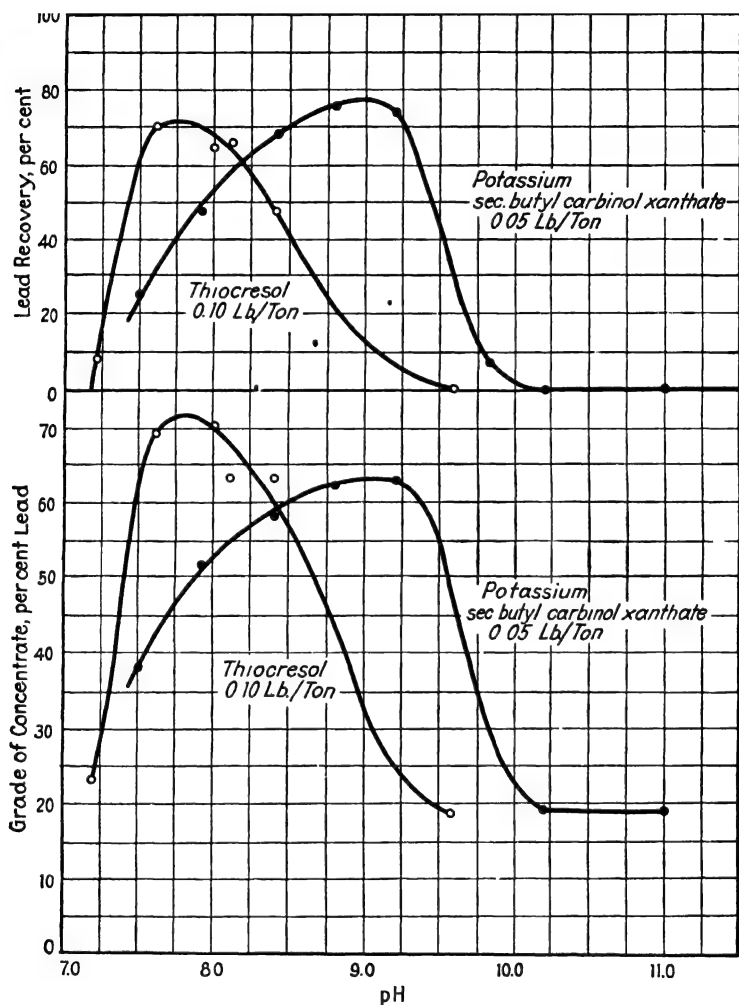


FIG. 80.—Cerussite-calcite separation.

Effect of variations in pH upon the floatability of cerussite from 1:4 mixtures with calcite (100/600 mesh) using potassium sec.-butyl carbinol xanthate, 0.05 lb. per ton, or p-thiocresol, 0.10 lb. per ton, together with terpineol, 0.20 lb. per ton, HCl or NaOH to suit. Pre-agitation, 45 seconds; flotation, 3 minutes.

Figure 78 affords a comparison of the effectiveness of xanthates having an aliphatic group in the hydrocarbon part of the molecule with others having an aromatic group.

Thiocresol is a very effective collector for cerussite, and probably also for other oxidized lead minerals (Fig. 79). Thionaphthol is about on a par with thiocresol but more difficult to use because of its lesser solubility in water. Thiophenol is less effective than thiocresol.

Figure 80 shows the effect of pH on recovery and grade of concentrate obtained from mixtures of cerussite and calcite sands<sup>(7)</sup> using amyl xanthate and thiocresol as collectors.

The use of amyl xanthate, 2.5 lb. per ton, in place of the same amount of ethyl xanthate on an oxidized ore resulted in a great improvement as may be judged from Table 94. In this instance, the use of amyl xanthate would have resulted in a saving of 34

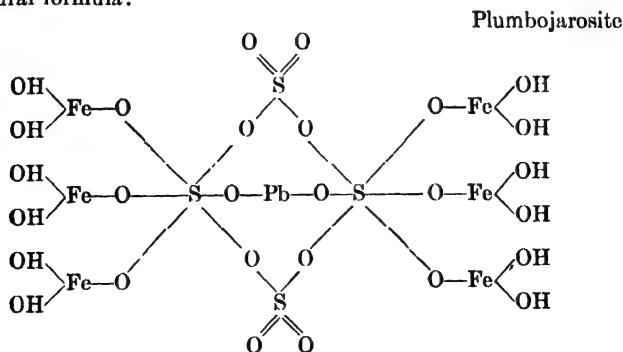
TABLE 94.—COMPARATIVE RESULTS OBTAINED ON OXIDIZED LEAD ORE THROUGH THE USE OF ETHYL AND AMYL XANTHATES (2.5 LB. PER TON)

Material	Lead, per cent		Lead recovery, per cent	
	Ethyl xanthate	Amyl xanthate	Ethyl xanthate	Amyl xanthate
Feed.....	15.2	15.2		
Concentrate...	55.1	58.3	82.2	93.6
Tailing	3.5	1.3		

lb. of lead per ton of ore worth (at 6 cts. per pound for refined lead) approximately \$1.40 at an additional cost of about 40 cts.

**Jarosites.**—The jarosites<sup>(14)</sup> have been found one of the chief causes of poor lead and silver recoveries in oxidized ores. The jarosites<sup>(12)(13)</sup> are complex basic sulfates<sup>1</sup> occurring in thin

<sup>1</sup>Structural formula:



hexagonal plates. The valuable metal may be lead, as in plumbojarosite; or silver, as in argentojarosite. At best they are low-grade minerals, plumbojarosite containing 19.7 per cent lead oxide, and argentojarosite 18 per cent silver oxide.

Plumbojarosite occurs as fine crystalline aggregates which, on grinding, give rise to thin plates averaging from 5 to 15 microns in diameter and 1 to 2 microns in thickness.

Plumbojarosite cannot be sulfidized and is not recoverable through the use of ethyl or amyl xanthates. Due to its flakiness considerable recovery can be obtained by mechanical overflow using a frother only. But such a method would not be practicable, as it would result in simultaneous recovery of much fine gangue. Plumbojarosite is collected by octyl and lauryl xanthates if the reagents are used in sufficient quantity (Fig. 81).

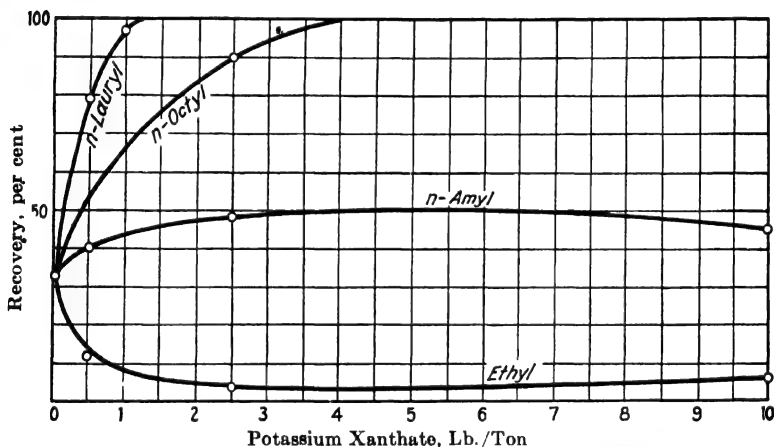


FIG. 81.—Plumbojarosite. (Communicated by D. A. Lyon.)

The mineral is collected by lauryl and octyl xanthates if they are used in sufficient quantity together with a sufficient amount of frother (terpineol, 0.5 lb. per ton).

### PRACTICE

According to Hahn<sup>(10)</sup> lead losses occur alike in very coarse and very fine particles. This is much the same as results in the treatment of all ores but is more marked in the case of the oxidized ores because oxidized minerals, even after sulfidizing, are not as floatable as sulfide minerals, and the deleterious effects of extreme coarseness or of extreme fineness are magnified. Furthermore, the relative proportion of the very fine particles is greater than in sulfide ores.

**Reagents.**—The reagents used in practice up to 1926 included a soluble sulfide for sulfidizing; sodium silicate (waterglass) to disperse the fine gangue particles, oily reagents such as P. and E. oil, Barrett No. 4 oil, Lewis tar, Eureka Metallurgical Company's No. 70, and wood creosote as collectors; pine oil and cresylic acid as frothers. More recently xanthates have been used as collectors in addition to sodium sulfide for sulfidizing and sodium silicate for gangue dispersion. Amyl xanthate is far superior to ethyl xanthate for this purpose, and its use has become standard in this field<sup>(3)</sup>. Some plants have retained the use of oils adding various chemical collectors at the same time.

**Results.**—Table 95 shows the results obtained in practice on various types of ores. The average selectivity index between

TABLE 95.—METALLURGICAL RESULTS OBTAINED ON OXIDIZED LEAD-SILVER ORES (1926-1927)  
(After Hahn.)

Mills	Metal content						Approximate selectivity index, lead to gangue
	Feed		Concentrate		Tailing		
	Ag, oz. per ton	Pb, per cent	Ag, oz. per ton	Pb, per cent	Ag, oz. per ton	Pb, per cent	
Shattuck Denn.....	6.8	6.1	40.2	39.0	1.6	0.55	12
Eureka Holly.....	2.5	10.0	25.0	55.0	1.2	2.2	9
San Diego.....	4.5	4.0	....	....	2.5	2.0	
American Smelting and Refining Company, Peru.....	55.0	1.0	....	....	3.0	Tr.	
Grand Central .....	4.5	5.8	14.0	33.0	3.3	2.8	4.5
Victoria Mine Bingham Mines Company.....	11.4	6.5	91.5	53.1	2.7	0.9	14.2

lead and gangue is about 9, that is very much below the selectivity indices obtained in the separation of galena from non-sulfide gangue in sulfide flotation (average 45).

**Undesirability of Conditioning.**—Conditioning of the pulp with sodium sulfide had long been considered a necessity. Recently, however, it has been pointed out that the sulfidized coatings wear out or oxidize in time. Introduction of the

sodium sulfide or other sulfidizing agent immediately ahead of the flotation cells or in the first cell of a battery of cells has become usual; in this way the mineral is coated and floated before there is time for sulfidizing to lose its effectiveness.

**Chief Consolidated Mill.**—Practical results obtained without sulfidizing at the Chief Consolidated mill have been described by G. H. Wigton<sup>(18)(19)</sup>. The ores milled by Chief Consolidated are from the Tintic District of Utah.

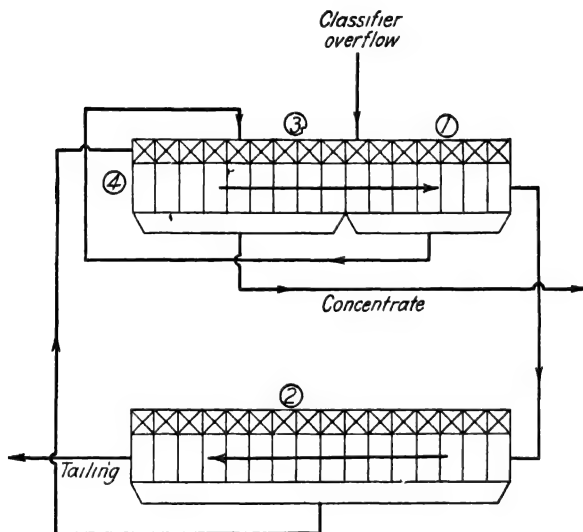


FIG. 82.—Flotation division, Chief Consolidated mill (oxidized ore).

The flow-sheet of the flotation division (Fig. 82) is typically a series arrangement of 32 M.S. sub-aeration cells fitted with 21-in. impellers. The pulp is directed from the classifier overflow to the tenth cell of the first sixteen-cell machine, and a concentrate is drawn from seven cells (tenth to sixteenth cells) ①. This concentrate is cleaned in the fifth to ninth cells of the same machine ③. The tailing from ① is floated further in sixteen cells ②, producing a final tailing and a rougher middling cleaned in the first four cells of the first machine ④. The concentrate from the first nine cells of the first machine is thickened and filtered.

In the laboratory the reagents used were aerofloat, acting partly as a frother and partly as a collector, ethyl xanthate as the main collector, and sodium silicate. These reagents were



used to the amounts of approximately 0.6, 5.0, and 3.0 lb. per ton, respectively. In the mill it was found necessary to reduce, then discontinue, the use of aerofloat because of the extremely voluminous froth that it produced; at the same time the amount of xanthate had to be increased.

More recently a new reagent called C-C has been used. The exact composition of C-C is unknown. Considerable latitude may apparently be exercised in its preparation which involves the mixing of amines, alcohols, and phosphorus pentasulfide.

Concerning the reagents used Wigton says:

As a comparatively large amount of aerofloat is needed to collect the oxidized minerals, its great frothing properties result in the production of a dirty, voluminous froth, if it is used without a modifying agent. The use of ethyl xanthate in the proper amounts along with the aerofloat results in the production of a desirable selective froth, heavily laden with the oxidized minerals. Too much xanthate will result in the production of a clean, brittle froth having a characteristic dry appearance, but too fragile to remove over the top of the cell.

In the mill it was found that ethyl xanthate had to be used up to 8 lb. per ton if no correction was made for the fact that the

TABLE 96.—METALLURGICAL RESULTS AT CHIEF CONSOLIDATED MILL (1928)  
(After Wigton.)

Material	Content								
	Au, oz. per ton	Ag, oz. per ton	Pb, per cent	Cu, per cent	Insol., per cent	Zn, per cent	Fe, per cent	CaO, per cent	S, per cent
Ore. ....	0.278	12.03	11.84	0.22	59.82	0.91	7.04	2.43	1.25
Concentrate. ....	0.617	36.66	38.85	0.48	21.76	1.42	5.49	4.50	3.04

Recoveries:

Gold . . . . .	64.33 per cent
Silver. . . . .	88.56 per cent
Lead. . . . .	95.34 per cent
Rejection of insoluble. . . . .	89.43 per cent
Ratio of concentration. . . . .	3.44 : 1

Selectivity indices:

Lead:insoluble. . . . .	13.1	Silver:insoluble. . . . .	8.1
Lead:lime. . . . .	4.2	Silver:lime. . . . .	2.5
Lead:iron. . . . .	8.4	Silver:iron. . . . .	5.1

pulp was somewhat more alkaline than in the laboratory. Keeping the pH in the range 6.8 to 7.2 was found vital to securing commercial results.

Table 96 shows the quality of the work done. Selectivity indices were calculated for the separation between lead and insoluble, iron and lime; likewise between silver and insoluble,

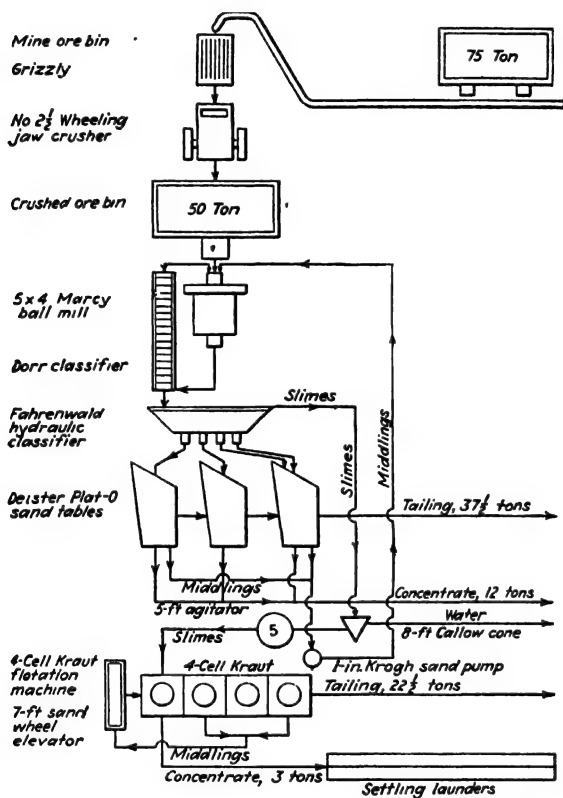


FIG. 83.—A 75-ton unit for the concentration of oxidized lead-silver ores. (After Druling.)  
Tabling and flotation.

iron and lime. It may be of more than passing interest to note the great disparity of the selection between lead and insoluble on the one hand, and between lead and lime on the other. The much greater difficulty in rejecting lime is obvious. It should also be mentioned that the selectivity indices between silver or gold and insoluble, lime, or iron are lower than the corresponding indices for lead.

**The Small Oxidized Lead-silver Mill<sup>(5)</sup>.**—Figure 83 presents a typical flow-sheet suggested for a small oxidized lead-silver flotation plant.

**Tabling as Adjunct to Flotation.**—In many instances it has proved advantageous to retain table concentration in connection with flotation for the treatment of oxidized lead ores. Tables remove a large portion of the lead as a relatively clean, coarse concentrate at low cost; at the same time the reagent consumption in the subsequent flotation operation is reduced because of the lessened amount of mineral to be floated, and because of reduced tonnage to be handled by flotation. As a result, the over-all recovery is often slightly increased.

**San Diego Mill<sup>(15)</sup>.**—The San Diego Mill, Santa Barbara, Mexico, illustrates concentration practice for oxidized ores in which tabling and flotation with collecting oils and sulfidizing are used.

The ore treated (700 tons daily) contains about 5 per cent lead and 5 oz. silver per ton. The lead is largely in the form of cerussite (60 per cent), but galena (20 per cent), anglesite (10 per cent), plumbojarosite (5 per cent), and other minerals are also found.

The ore is crushed, ground, classified, tabled, and floated. Tabling makes a final tailing and a middling. The reground table middling together with the primary slime constitutes the flotation feed. The flotation division involves three roughing stages in series and one cleaning stage, the cleaner tailing returning to the head of the second rougher.

Reagents used are as per Table 97.

TABLE 97.—REAGENTS USED AT SAN DIEGO OXIDIZED LEAD MILL  
(After Monk and Weiss.)

	Lb. per Ton
Crude oil. . . . .	1 47
Pine oil. . . . .	0 37
Cresylic acid. . . . .	0 28
Wood-tar creosote . . . . .	0 25
Gasoline and kerosene . . . . .	0 16
Sodium sulfide. . . . .	4 0
Sodium silicate (dry). . . . .	0 8

## COPPER ORES

Although the flotation of oxidized copper ores has not advanced much beyond the experimental stage, the results obtained so far

are of decided interest. Just as in the case of oxidized lead ores, there are marked differences in the behavior of the different minerals involved; the two carbonates are the most readily floated, then come the oxides, and last the silicates. Considerable work has been done in connection with the flotation of the carbonates, less with that of the oxides, and very little with that

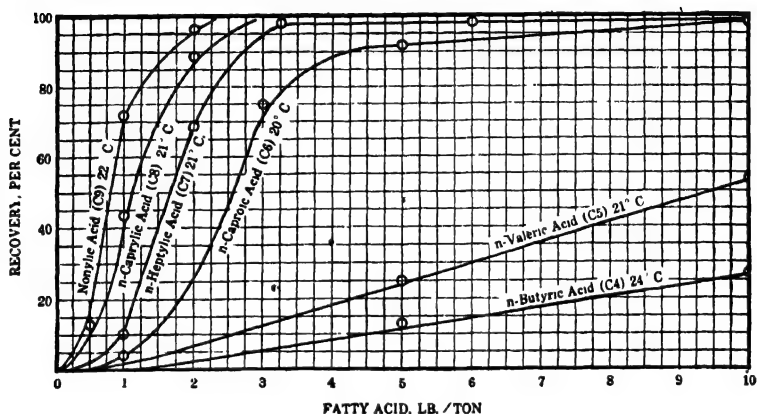


FIG. 84.—Malachite flotation with saturated fatty acids. Mineral, 100/600 mesh.

of the silicates. Again, as in the case of the flotation of oxidized lead minerals, oxidized copper minerals can be made floatable by three methods: (1) by the use of fatty acids and soaps, (2) by sulfidizing, together with the use of sulfide-copper collectors, and, (3) by direct flotation with sulfide-copper collectors.

**Fatty Acids and Soaps.**—The copper carbonates are floated by higher fatty acids and soaps (Fig. 84). Azurite is more readily floated than malachite, the difference in behavior between the two carbonates being particularly marked if the hydrocarbon chain of the fatty ion is short. Indeed, butyric and propionic acid used in large amount can be used to separate the two carbonates. This remarkable effect is unexplained and appears still more mysterious when it is noted that it is substantially impossible to separate malachite or azurite from calcite with fatty acids. A greater difference in behavior would naturally be expected between malachite and calcite than between malachite and azurite; yet this does not appear to be the case.

Although it has been found impossible to separate malachite (or azurite) from calcite through the use of fatty acids—which

can be interpreted by assuming that soluble copper and calcium salts mutually affect the surfaces of the two minerals—the separation of malachite from pure quartz is readily achieved. This may explain the effectiveness of soaps (particularly those of palmitic, oleic, and stearic acids) in the treatment of some oxidized copper ores. Table 98 shows the results obtained in

TABLE 98.—SEPARATION OF DESLIMED MALACHITE FROM QUARTZ IN 1:4 SYNTHETIC MIXTURES

Reagents		Time of preagitation, minutes	Temperature, degrees centigrade	Copper recovery, per cent	Copper in concentrate, per cent	Selectivity index
Terpincol, lb. per ton	Sodium oleate, lb. per ton					
0 20	0 02	0 5	20	90	46.4	9 5
0 25	0 02	1 5	20	88	42.6	8 1
0.25	0 03	1	20	94	38.4	12 6
0 25	0 03	0 75	20	96	32.1	9 5
0.30	0.10	2	20	93	20.3	3 8

the separation of synthetic mixtures of malachite and quartz through the use of sodium oleate. It is likely that the results can be improved through careful control of the pH and through the use of sodium silicate.

Oxidized (carbonate) copper ores are concentrated by flotation in the Katanga region through the use of palmitic acid (2.0 lb. per ton)<sup>(1)</sup>.

A few pilot experiments to determine the floatability of chrysocolla with oleic acid and sodium oleate have indicated that the mineral can be collected. This is in agreement with the fact that quartz, previously activated by a copper salt, is readily floated by soaps. Quartz treated with copper salts abstracts cupric ion and may therefore have a surface similar to that of chrysocolla. The separation of chrysocolla from quartz appears more difficult than the separation of malachite from silica. Although some positive indications have been obtained in the laboratory, it cannot be said that the problem is solved.

**Sulfidizing.**—It seems to have been generally accepted that oxidized copper minerals ought to be readily sulfidized because of the very great insolubility of copper sulfides. However, the

sulfidizing of copper silicate is practically impossible, and that of malachite and azurite is much slower and less satisfactory than the sulfidizing of cerussite or anglesite.

Table 99 presents some results, perhaps exceptional, obtained on a quartzitic carbonate copper ore<sup>(11)</sup>, using as reagents sodium sulfide, 4.0 lb. per ton, amyl xanthate, 0.30 lb. per ton, aerofloat No. 25, 0.45 lb. per ton, and sodium silicate (dry), 0.20 lb. per ton.

TABLE 99.—FLOTATION OF QUARTZITIC MALACHITE ORE (1930)  
(After Hahn.)

Product	Copper content, per cent	Recovery, per cent
Feed	1 74	72.0
Cleaner concentrate	25 86	
Cleaner tailing	2 93	
Rougher tailing	0.44	

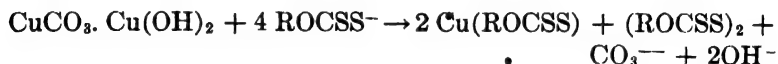
A few experiments conducted by A. E. Anderson have indicated that the floatability of copper minerals after sulfidizing, if floated with the same collectors as are used in the flotation of sulfide minerals, is slightly less than the floatability of the same minerals without sulfidizing. Until positive evidence has been adduced of the value of sulfidizing in the treatment of oxidized copper ores, it would seem best to investigate in every case the relative merits of sulfidizing and direct flotation with sulfhydrylate collectors.

**Direct Flotation with Xanthates, Mercaptans, and Other Organic Collectors.**—Concentration by flotation of carbonate copper ores can be accomplished through the use of ionizable reagents forming highly insoluble copper salts and possessing a substantial non-polar portion in their makeup if the ores have a small content of carbonate-copper slime. It is believed that the reagents that are effective on copper carbonates would also be effective on copper oxides, but they have failed with copper silicates.

The effect of organic sulfhydrates is to form, by double decomposition with the mineral, certain very floatable crusts at the mineral surface. In order for flotation to proceed, the reaction

has to be carried sufficiently to produce a relatively thick coating. Microscope examination leaves no doubt that the coating is irregular in thickness, apparently having grown preferentially at certain spots. Figure 6, Chap. V, shows the coating formed at the surface of azurite by amyl xanthate. The coating was produced under experimental conditions representing an exaggeration of natural conditions. In Fig. 6, the upper left portion represents the untreated azurite surface and the lower right the same surface after treatment with xanthate solution. Crystalline outlines appear in this portion of the figure. They may be copper xanthate.

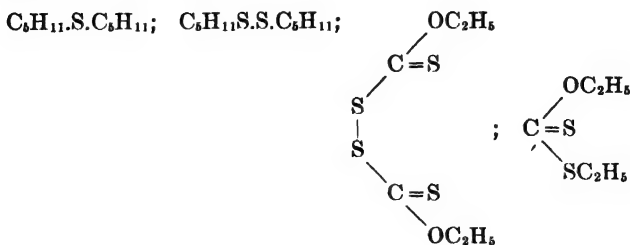
The reaction between the dissolved xanthate and the mineral is probably as follows:



Among the reagents that float malachite in a manner similar to the higher xanthates may be mentioned certain amines, the reaction products of amines and carbon disulfide (dithiocarbamates), certain hydrazines (as phenylhydrazine), trithiocarbonates (reaction products of mercaptans with carbon disulfide and alkali), mercaptans, thiophenols and thionaphthols. It is of interest to note that non-ionized compounds, in other respects similar to the above, fail completely where ionized compounds succeed. Thus, amyl sulfide, amyl disulfide, ethyl dixanthogen, ethyl-ethyl xanthate<sup>1</sup> do not float malachite, whereas amyl mercaptan and ethyl xanthate (in large quantity) do.

The most effective of the many reagents tried<sup>(7)(8)</sup> are, in order of decreasing effectiveness: amyl mercaptan, benzyl mercaptan, butyl mercaptan, thio-beta-naphthol, amyl xanthate. Broadly speaking, then, mercaptans are the most effective, the aryl hydrosulfides (thiophenols and thionaphthols) are next

<sup>1</sup> Formulas are as follows:



and the xanthates third. Figures 85, 86, and 87 show the effect of various xanthates, mercaptans, and aryl hydrosulfides on the flotation of malachite.

The main objection to the use of the higher xanthates, mercaptans, or thiophenols in the flotation of the carbonate copper ores is that much reagent is required, and that the reagents are

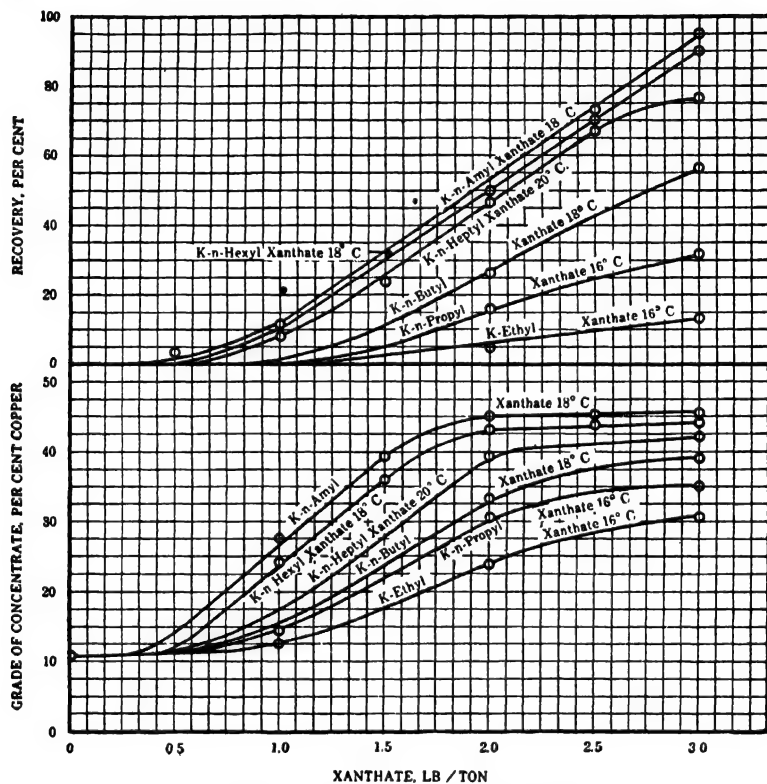


FIG. 85.—Malachite-calcite separation.

Flotation with potassium xanthates. (1:4 mixtures; 100/600 mesh.)

not cheap. In fact the situation is more adverse than might be thought by a casual examination of Figs. 85 to 87, because the curves present results obtained with a deslimed charge of pure minerals in which the conditions are idealized. In practice considerably more reagent would no doubt be required, perhaps 5 to 10 lb. per ton of ore. At 25 cts. per pound, the reagent cost appears prohibitive when compared with the usual reagent cost. Since chemical collectors do not collect silicate copper, which is often associated with carbonate copper, and since



leaching methods (ammonia or sulfuric acid) are available for the treatment of carbonate and silicate copper ores, the field of flotation by chemical collectors is much restricted.

In order to reduce the cost of the reagent in the flotation of carbonate copper ores a study of activating agents was made<sup>(7)</sup>

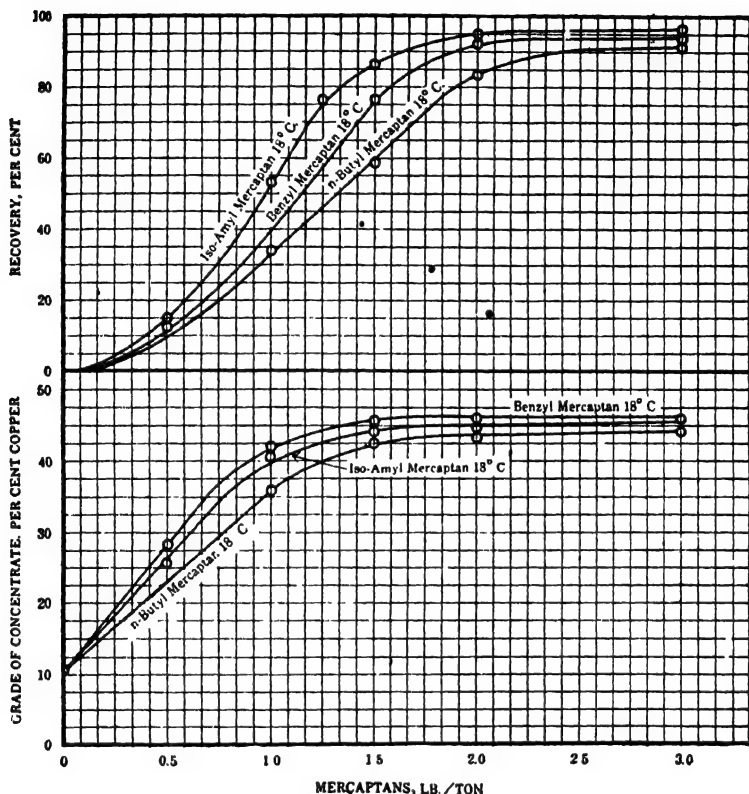


FIG. 86.—Malachite-calcite separation.  
Flotation with mercaptans. (1:4 mixtures; 100/600 mesh.)

which led to the conclusion that, if properly employed, lead and zinc salts can be of use (Fig. 88). In preliminary tests on pure minerals, it was found possible to reduce the collector consumption by approximately 40 per cent at a trifling additional cost for the activating salt.

**Industrial Application.**—At Kennecott<sup>(4)</sup> a semi-oxidized ore is treated by a combination of gravity concentration, ammonia leaching, and flotation. Gravity concentration recovers the coarse copper sulfides and a little of the carbonates; leaching

extracts the carbonate copper remaining in the coarse gravity-concentration tailings, and flotation recovers some of the copper in the fine gravity-concentration tailings and "primary slime."

The flow-sheet of the flotation division is that of a simple rougher-cleaner circuit; reagents are sodium sulfide, 3.0 lb. per

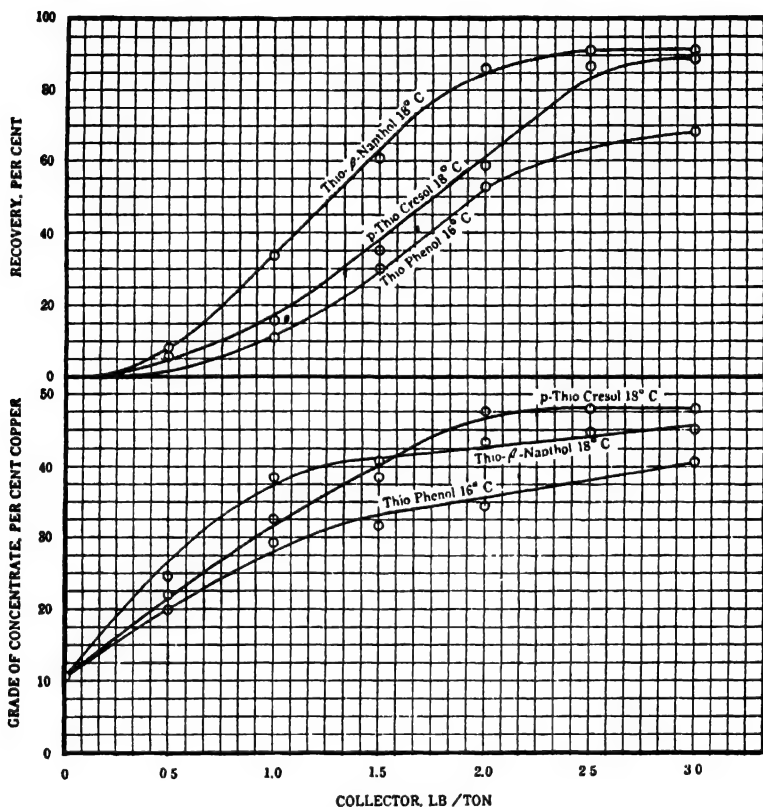


FIG. 87.—Malachite-calcite separation.

Flotation with aromatic hydrosulfides. (1:4 mixtures; 100/600 mesh.)

ton; calcium polysulfide, 1.2 lb. per ton; coal-tar creosote, 1.40 lb. per ton; and steam-distilled pine oil, 0.30 lb. per ton. Recovery of copper (azurite, malachite, and a little chalcocite) averages 75 to 80 per cent from a feed averaging 3 per cent. The concentrate contains about 30 per cent copper. Copper losses are greatest in the finest sizes.

**Flotation of Metallized Oxidized Copper Ores.**—Concentration by flotation of metallized oxidized copper ores has been proposed. Laboratory results have been satisfactory but the practical value

of such a treatment has to be demonstrated, particularly in view of the relatively costly pyrometallurgical operation which must precede flotation.

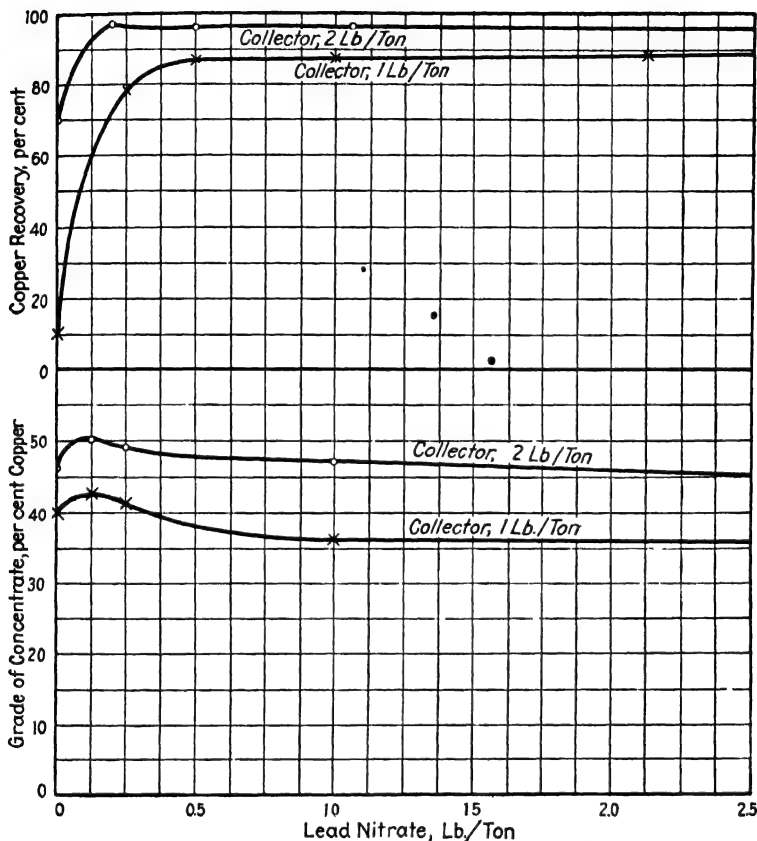
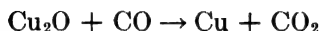
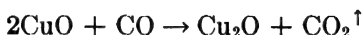


FIG. 88.—Malachite-calcite separation.

Activating effect of lead nitrate using potassium sec.-butyl carbinol xanthate as collector, and terpineol, 0.20 lb. per ton as a frother. The charges (1:4 mixtures, 100/600 mesh) were conditioned with lead nitrate for 2 minutes, then twice washed with distilled water and decanted. Pre-agitation 45 seconds; pH range, 9.0–9.6; temperature 18 to 21°C.

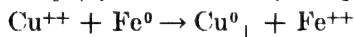
Broadly speaking, the scheme consists in (1) crushing the ore, (2) subjecting the ore to a reducing heat treatment to decarbonize and deoxidize the copper minerals, (3) grinding the reduced ore to flotation size, and (4) floating with the reagents customarily employed in native-metal flotation.

The reduction involves the following stages:



Reduction need not be complete, as surface metallization of the mineral particles is said to be sufficient, in spite of the subsequent grind, to permit ready collection of the copper-bearing minerals.

**Leaching-flotation Schemes.**—It has been proposed to leach oxidized copper ores with sulfuric acid, add fine scrap iron to precipitate copper, and float the pulp (after grinding, if necessary) for the extraction of copper. The reactions involved are:



The advantage claimed for this treatment scheme is the elimination of the elaborate and costly filtering division of leaching plants, and the replacement of a large first cost in a leach-filtering plant by a low first cost but higher operating cost in a flotation plant. If the process has economic merits, they are undoubtedly largest for large plants operating on a low-grade ore and having low-cost power.

## ZINC ORES

Up to now, no success has been had in the treatment of oxidized zinc ores by flotation; it is true, however, that little work has been done toward the solution of the problem because of the lack of demand for zinc ores and concentrates. Of the two common oxidized zinc minerals, it is clear that smithsonite, the carbonate, can be recovered more readily either through the use of soaps or through direct flotation with long-chain xanthates and mercaptans. Calamine, on the other hand, presents a problem analogous to that presented by chrysocolla. Besides, pure calamine would be industrially undesirable. Table 100 presents the results of some pilot work done on the flotation of mixtures of zinc carbonate (contaminated by iron and manganese apparently in solid solution) with calcite by means of long-chain xanthates and hydrosulfides. Although the results presented

TABLE 100.—FLOTATION OF SMITHSONITE\* FROM 1:4 MIXTURES WITH CALCITE

Reagents, lb per ton				Metal content			Percentage recovery in		Smithsonite-calcite selectivity index, roughing
				Zinc, per cent					
Octyl† xanthate	Thio-cresol	Amyl mer-captan	Heptyl mer-captan	Concen-trate	Mid-dling	Tailing	Concen-trate	Mid-dling	
4.0	...	.		32.7	6.2	1.1	53.7	39.0	3.9
6.0	..	.		18.8	1.5	0.8	90.6	7.1	4.1
8.0	.	.		9.4		0.76	97.5		4.1
	2.0			22.8		5.8	28.6		3.0
	4.0			21.0.		3.7	60.2		3.5
	8.0			22.4	..	1.9	80.3		5.4
		1.0		9.9		6.8	25.8		1.3
		2.0		21.4		3.7	61.2		3.4
		3.0		22.5		1.8	81.7		5.6
		4.0		32.1		1.3	85.3		14.7
			2.0	33.2	..	1.3	85.5		17.2
			4.0	30.5		0.22	97.8		30.6
			8.0	31.6		0.28	97.0		30.0

\* The Smithsonite used in these experiments was an impure, though crystalline, manganiferous and ferruginous variety.

† Over-frothing was observed when using octyl xanthate.

in this table should not be construed as any more than preliminary, they indicate definitely that zinc carbonate can be collected from other associated carbonates through the use of certain definite chemical collectors.

### SELECTIVE FLOTATION OF MIXED BASE-METAL CARBONATE ORES

**Lead-copper.**—Although the separation of oxidized lead from oxidized copper minerals would appear difficult at first sight, rather remarkable results can be obtained through the use of well-chosen collectors and depressing agents.

Aliphatic mercaptans, such as amyl mercaptan, favor the flotation of copper carbonate over that of lead carbonate (this is in agreement with the data obtained in separating cerussite from calcite and malachite from calcite), but the higher xanthates favor the flotation of lead carbonate over that of copper carbonate, as likewise thiocresol. These collectors may therefore be considered to be to some extent selective collectors for the carbonates of lead and copper. It should be noted that they are also selective collectors for the sulfides of the same metals and

therefore can form the basis of better selective flotation of the sulfides of lead and copper.

Certain inorganic salts can be added to increase substantially the selective action between lead and copper carbonates. Among these are certain selective solvents, such as cyanides, which keep the soluble mineral in a wetted state until the solvent is used up; also, certain coating agents which compete for the surface of the mineral to be inhibited with the collecting agent. Thus chromates, phosphates, arsenates form insoluble coatings at the surface of cerussite, but to a lesser extent at the surface of malachite; they can therefore be used to inhibit the lead mineral while the copper mineral is floated. The difference between the effects of cyanide at the surface of malachite and of chromate at the surface of cerussite is that one reagent is affecting the surface of the lead mineral permanently while the other is affecting the surface of the copper mineral temporarily.

Table 101 shows that truly remarkable results can be obtained.

TABLE 101.—SELECTIVE FLOTATION RESULTS ON COPPER AND LEAD CARBONATES (1-1-3 MIXTURES OF MALACHITE, CERUSSITE, AND CALCITE)

Reagents, lb. per ton						Recoveries, per cent		Selectivity indices	
Amyl xanthate	Ethyl xanthate	Amyl mercaptan	Thio-cresol	Ammonium phosphate	Sodium cyanide	Cu	Pb	Pb : Cu	Cu : Pb
	.	2 0	.	..		39	1 6	..	6.3
	.	3 0				66	2 9		8 2
	.	4 0				77	3 7		9.4
	.	5 0				85	3 7		12.1
	.	4.0		1 0		90	0 4		47
			1 0			18	80	4 3	
	3.0					12	94	10 7	
1 0	.					14	35	1 8	
	.		1 0		1 0	2 1	99	67	

**Copper-zinc.**—Table 102 presents some results in the separation of malachite from smithsonite.

**Lead-copper-zinc.**—From Tables 101 and 102 it is apparent that if xanthates are used as collectors, the floatability of the carbonates of lead, copper, and zinc decreases in the order lead, copper,

TABLE 102.—SELECTIVE FLOTATION OF MALACHITE FROM SMITHSONITE WITH REAGENTS CAPABLE OF FLOATING SMITHSONITE (FROM 10-10-30 MIXTURES OF MALACHITE, SMITHSONITE, AND CALCITE)

Reagents, lb. per ton				pH of rougher tailing	Recoveries, per cent, in						Selectivity indices			
Amyl mercaptan	Heptyl mercaptan	Sodium hydroxide	Sodium cyanide		Concentrate		Cleaner tailing		Roughing, in favor of		Cleaning, in favor of			
					Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn		
2 0	.	.	.	.	43.7	14.5	33.7	25.4	2.3	....	1.5	....	1.25	
4.0				.	71.2	17.8	15.2	29.3	2.7	....	2.8	....	1.25	
...	2 0	.	.	.	9 0	17.4	16.0	18.5	....	1.25	...	1.0	1.25	
...	3 0	.	.	.	18 7	23.8	37.1	33.6	1.0	1.0	...	....	1.4	
...	4 0	.	.	7.7	52 8	30.8	45.5	49.6	3.8	....	1.4	....	3.7	
...	6 0	.	.	....	71.1	47.6	26.5	32.5	3.2	....	1.4	....	4.8	
...	16 0	...	.	.	98 3	74 0	1 1	11.9	5.6	....	1.7	....	1.3	
...	4 0	0 25	.	8 0	73.2	43.2	23.4	39.0	2.3	....	1.7	....	1.3	
...	4 0	2 0	.	10 7	95.4	31.6	3 7	28.1	8.6	....	4.8	....	1.3	
...	4 0	5 0	.	12 0	99.8	33.0	0 2	67.0	31.6	....	1.3	....	1.3	
...	4 0	.	4 0	8.9	69.7	52.0	15 0	17.7	1.6	....	1.3	....	1.3	

zinc. This is also shown by Table 103 which presents some test results obtained on a mixed carbonate ore from Nevada.

TABLE 103.—SELECTIVE FLOTATION OF OXIDIZED LEAD-COPPER-ZINC ORE

Test number	Product	Metal content			Recoveries, per cent			Selectivity indices		
		Pb, per cent	Cu, per cent	Zn, per cent	Pb	Cu	Zn	Pb : Cu	Pb : Zn	Cu : Zn
1	Feed . . .	6.7	3.2	20.3						
	Concentrate . . .	33.9	10.4	6.476	48	4.6		1.85	8.1	4.4
	Tailing . . .	1.9	2.0	23.6						
2	Concentrate . . .	37.7	17.0	7.393	28.8	4.5	5.7	1.35	15.1	11.1
	Tailing	0.55	0.45	23.5						

## Reagents.

Test 1: amyl xanthate, 3.0 lb. per ton, and pine oil, 0.2 lb. per ton.

Test 2: amyl xanthate, 6.0 lb. per ton, and pine oil, 0.2 lb. per ton.

Marked segregation is obtained of lead and copper from zinc, indicating that the relative floatabilities of the lead and copper carbonates are nearer each other than either is to that of zinc carbonate. This is in agreement with the results obtained in sulfide flotation.





## CHAPTER XII

### PRECIOUS AND RARE METALS

In this chapter is discussed the treatment by flotation, or by flotation in combination with other treatment methods, of ores of gold, silver, platinum, mercury, and molybdenum occurring in the native, sulfide, selenide, or telluride form.

#### GOLD AND SILVER

**Mineralogical Occurrences.**—Gold occurs native, as a telluride, or in an unknown form in close association with base-metal sulfides particularly pyrite, chalcopyrite, and arsenopyrite<sup>(22)</sup>.

Silver occurs native, as the sulfide or selenide, in gold tellurides, as sulfarsenides or sulfantimonides, replacing copper in tetrahedrite and tennantite, and in an unknown form in close association with base-metal sulfides, particularly galena, chalcopyrite, and arsenopyrite<sup>(6)</sup>.

The variety of forms in which gold and silver occur in unoxidized ores, together with the very small content of the minerals sufficient to make ore out of waste, is responsible for the poor state of our knowledge of the mineralogical occurrence of the precious metals.

**Present Status of Flotation.**—In recent years cyanidation and amalgamation have been the basic methods employed to extract gold from its ores. The use of flotation has been relatively small. This has been due in no small part to the fact that no new gold fields of importance have been developed since flotation attained its full industrial stature. In addition to its own amortization charges, flotation would have to incur the relatively large amortization cost of cyanidation, if it were to replace that older process. As new gold fields are developed it is likely that flotation will play an increasing part in the treatment of certain gold ores, either in place of, or in conjunction with, cyanidation.

For the treatment of silver ores, flotation has been of greater importance, partly because silver is generally well recovered by

flotation, but also because cyanidation and amalgamation are not so effective in extracting silver as in extracting gold.

**Ore Types.**—Gold and silver production comes from four main sources:

1. As by-products from the treatment of base-metal ore in which the precious metals are largely incidental.

2. From ores in which the value of the precious metals is of the same order of importance as the value of the base metals.

3. From ores in which the base metals account for but a minor portion of the total value of the ore, but in which a substantial bulk of sulfides exists.

4. From ores in which the base metals account for but a minute portion of the total value of the ore and in which there is but a small bulk of sulfides.

Ores of the first type present no special features of treatment as compared with straight base-metal ores other than the desirability of collecting the gold and silver in the lead or copper concentrate rather than in the zinc concentrate. Recovery of gold in the lead or copper concentrate is sometimes difficult to achieve as gold is frequently associated with pyrite; if this pyrite is rejected in the tailing a considerable portion of the gold is lost, too. In one instance at least (Chap. X, page 261) it has been found profitable to cyanide the flotation tailing for gold extraction. In other cases a pyrite concentrate containing gold has been made for flux in lead smelting (Chap. IX, page 239).

Ores of the second type, that is, in which the value of the base metals is of the same order of magnitude as that of the precious metals, are typified by gold-copper and silver-lead ores. Gold-copper ores necessitate flotation as part of the treatment scheme. Many silver-lead ores contain considerable zinc, too, so that their treatment is essentially one of selective flotation yielding a lead-silver and a zinc concentrate (Chap. IX, page 238).

Ores containing no substantial bulk of base metals but considerable sulfides are typified by pyritic and arsenical gold ores. They lend themselves readily to concentration by flotation. If dispersion of the gold in the sulfides is not on too fine a scale, they can also be treated by cyanidation, so that these two processes are to some extent in direct competition on ores of this type.

Precious-metal ores containing no substantial bulk of base metals or of sulfides are better suited to treatment by cyanidation or amalgamation than to treatment by flotation.

## GOLD-COPPER ORES

Gold-copper ores<sup>(2)</sup> necessitate a somewhat different treatment from copper ores in which the precious metals are of secondary importance. This because gold is often associated with pyrite or pyrrhotite as well as with the copper mineral (chalcopyrite).

Cyanidation of gold-copper ores yields poor gold extraction, and no copper recovery. The cyanide consumption is high. Collective flotation of the sulfides gives a voluminous low-grade concentrate. Selective flotation of chalcopyrite from the pyrite or pyrrhotite results in a poor recovery of the gold.

According to Godard and Parsons<sup>(9)(13)(8)</sup> proper treatment involves a combination of flotation with cyanidation, amalgamation, or gravity concentration. The following examples are illustrative.

**Example 1.**—A gold-copper ore containing Au, 0.34 oz. per ton; Cu (as chalcopyrite), 1.22 per cent; and iron (as chalcopyrite and pyrite), 8.69 per cent, was treated by collective flotation and by selective flotation. Typical results are presented in Table 104.

TABLE 104.—COMPARISON OF COLLECTIVE WITH SELECTIVE FLOTATION IN THE CONCENTRATION OF A PYRITIC GOLD-COPPER ORE  
(After Parsons.)

Treatment	Product	Weight, per cent	Metal content		Recovery, per cent	
			Copper, per cent	Gold, oz. per ton	Copper	Gold
Selective.....	{ Concentrate	9.0	11.36	1.22	91.9	37.6
	{ Tailing	91.0	0.10	0.20		
Collective.....	{ Concentrate	23.6	4.76	1.12	98.7	89.7
	{ Tailing	76.4	0.02	0.04		
Feed. ....	.....	.....	1.22	0.34		

Clearly, all the gold is not associated with the chalcopyrite, approximately two-thirds occurring with the pyrite or free; that the gold not recovered by selective flotation does not occur free is shown by the non-amalgamation of the unrecovered gold.

In the case of ores of this type, high recovery of both metals can be obtained by making a collective concentrate of low grade,

or by making two selective concentrates one high in copper for shipping and the other low in copper for cyanidation in either the raw or roasted condition.

**Example 2.**—A gold-copper ore containing gold, 1.06 oz. per ton; copper (as chalcopyrite), 2.21 per cent; and iron (largely as pyrite), 11.23 per cent, was found to be partly amenable to amalgamation, cyanidation, and flotation. Amalgamation recovered up to 70 per cent of the gold at a low cost; cyanidation from 93 to 96 per cent of the gold following fine grinding and with high cyanide consumption (8 to 12 lb. per ton); flotation from 65 to 70 per cent of the gold and about 90 per cent of the copper.

By combining flotation with cyanidation, that is by cyaniding the flotation tailing, it is possible to increase the gold extraction to 98 per cent and at the same time decrease the cyanide consumption to less than 4 lb. per ton of ore. Typical results are presented in Table 105.

TABLE 105.—FLOTATION OF GOLD-COPPER ORE FOLLOWED BY  
CYANIDATION OF THE TAILING  
(After Godard.)

Product	Weight, per cent	Metal content		Recovery, per cent	
		Au, oz. per ton	Cu, per cent	Au	Cu
Feed . . . . .	.....	1 21	2 21		
Flotation-cleaner concentrate .	6.6	12 5	30 6	68 3	90.3
Flotation-cleaner tailing (to be circulated). . . . .	2 0	5 97	2.96	9.8	2.7
Flotation-rougher tailing	91 4	(0 29)	0 17	. .	7.0
Cyanide leach from rougher tailing . . . . .	.....		.....	19 9	
Cyanide residue. . . . .	.....	0.025	.....	2 0	

**Example 3.**—A gold-copper ore containing gold, 0.78 oz. per ton (about nine-tenths free); copper (as chalcopyrite), 0.40 per cent; and iron (largely as pyrite), 1.67 per cent, yielded good recoveries of the copper but not of the gold when treated by flotation. This is shown by two tests recorded in Table 106.

Substantial additional gold recoveries could be made on the tailing by tabling. In the two tests recorded in Table 106, the

TABLE 106.—FLOTATION OF GOLD-COPPER ORE CONTAINING  
CONSIDERABLE FREE GOLD  
(After Godard.)

Test number	Product	Metal content		Recovery, per cent	
		Au, oz. per ton	Cu, per cent	Au	Cu
1	Concentrate	7.84	8.36	56.5	92.6
	Tailing	0.27	0.03		
2	Concentrate	11.13	10.71	54.3	89.4
	Tailing	0.32	0.04		

gold recovery was boosted to 91.9 and 90.5 per cent respectively, by tabling.

Amalgamation of the pulp before flotation resulted in even better over-all recoveries, the gold recovery rising in one instance to 97.6 per cent.

**Flotation of Native Gold.**—It might well be thought that if gold occurs free in the native state, it should float as well as other native metals. However, gold is malleable and becomes flattened to thin pellets in course of grinding; grinding does not comminute the gold particles but simply flattens them. It is therefore very difficult to reduce coarse gold flakes to a floatable size. Furthermore, such attempts would be uneconomical in view of the readiness with which they are recovered by gravity concentration or amalgamation.

Leaver and Woolf<sup>(11)</sup> made a study of the recovery by flotation of native gold occurring in copper ores. They come to the conclusion that much of the gold in the porphyry ores of the western United States occurs in the native state. The recovery of gold is markedly affected by the pH of the pulp, being greatest in the range pH 7 to 9. High-lime circuits, such as are used in many ores to inhibit pyrite, result in an inhibition of free gold. Evidence for this conclusion is adduced from the behavior of free-gold particles in circuits of various alkalinities.

**Tul-mi-chung Mill.**—Flotation of a gold-copper ore has been practiced at the Tul-mi-chung mill<sup>(21)</sup> of the Seoul Mining Company in Korea (Chosen). The gold together with some silver occurs in close association with chalcopyrite, pyrite, arsenopyrite, and lollingite.

The flow-sheet is as shown in Fig. 89 (1923). The overflow from the Dorr classifiers in closed circuit with the ball mills is divided by a two-compartment spitzkasten ① into a sand which is reground in a 5- by 5-ft. ball mill ②, in closed circuit, and an overflow feeding an eight-cell Lemmon-Hebbard sub-aeration flotation machine ③. Cells 1 to 6 produce a rougher concentrate and cells 7 and 8 a middling which is returned at the head

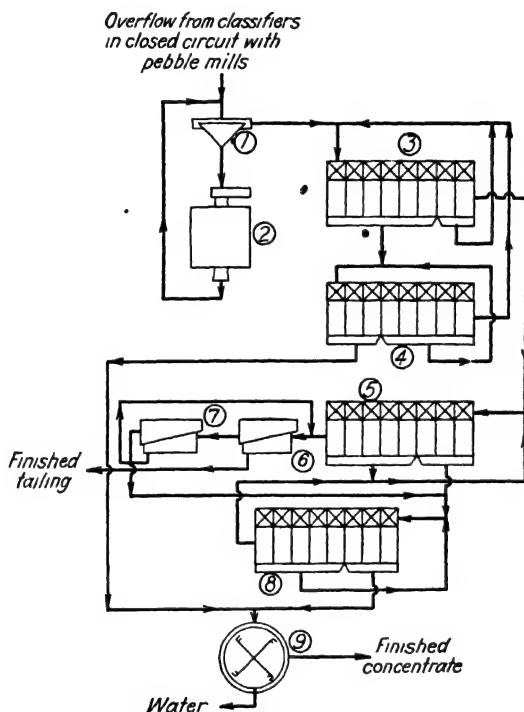


FIG. 89.—Flotation division, Tul-Mi-Chung mill.

of the machine. The concentrate is cleaned in a similar eight-cell machine ④, the first three cells producing a finished concentrate and the last five a middling which is returned at the head of the machine. The cleaner tailing is returned to ③.

The tailing from ③ is sulfidized and floated in an eight-cell Lemmon-Hebbard machine ⑥, yielding a secondary rougher concentrate from the first three cells and a middling from the others. The middling is returned to the head of the machine. The tailing is treated further in four Callow cells ⑥, before

discarding. The concentrate from the Callow cell is cleaned in one additional Callow cell (7), then recleaned with the concentrate from the first three cells of (5) in an eight-cell Lemmon-Hebbard sub-aeration machine (8) arranged as above.

Reagents used were as per Table 107, and metallurgical results as per Table 108.

TABLE 107.—REAGENTS AT TUL-MI-CHUNG (1923)

Reagent	Amount, lb. per ton	Place of addition
Caustic soda . . . . .	1 0	Primary grinding mill
Soda ash . . . . .	1 0	Primary grinding mill
Eucalyptus oil . . . . .	0 3	Primary grinding mill
Crude petroleum . . . . .	0 25	Secondary ball mill (2)
Sodium sulfide . . . . .	0 5	Head of third sub-aeration flotation machine (5)
Sodium silicate . . . . .	1 0	Head of fourth sub-aeration flotation machine (8)

TABLE 108.—TYPICAL METALLURGICAL RESULTS AT TUL-MI-CHUNG

Product	Metal content		Approximate recovery, per cent	
	Cu, per cent	Au, oz. per ton	Cu	Au
Feed . . . . .	1 0	0.30		
Concentrate . . . . .	20.0 to 24.5	5.0 to 5.4	90	70
Tailing . . . . .	0 10	0 09		

**Summary.**—The treatment of gold-copper-iron ores indicated by recent work is as follows.

1. If the gold is entirely associated with the copper sulfides or free and fine, selective flotation of the copper mineral at a low pH collects the gold in the copper concentrate.

2. If the gold is associated with the sulfides, partly with the copper minerals and partly with otherwise worthless iron sulfides several alternative flotation schemes can be followed. One alternative is to produce a low-grade collective concentrate. This is attractive if the iron content of the ore is not too high.



Another alternative is to make a selective copper concentrate and a copper-free sulfide-gold concentrate, with subsequent cyanidation of the raw or roasted copper-free concentrate.

3. If the gold is partly associated with the copper minerals and the rest is free and coarse, amalgamation of the pulp before flotation should be used.

4. If the gold is partly associated with the copper minerals and the rest is finely dispersed in the non-sulfide gangue, flotation followed by cyanidation of the flotation tailing is the logical treatment.

It is understood of course that definite choice of ore treatment should be made only after careful consideration of all the peculiarities of each ore.

In using flotation for the treatment of copper-gold ores the same considerations prevail as in the treatment of copper ores, with the added consideration that more attention should be devoted to securing a high recovery of gold and copper rather than a separation of copper from iron: putting it in common parlance, recovery is more important than grade. As a result frothing and collecting agents may be used more freely and iron-inhibiting reagents more sparingly than in the treatment of copper ores in which precious metals form but a secondary contribution to the total value of the ore.

### PYRITIC GOLD ORES

In some pyritic gold ores the gold occurs in the native state finely dispersed within the pyrite, so that good results are obtained by cyanidation, and then only if fine grinding is practiced. If the association of gold with pyrite is extremely intimate the ore may indeed be refractory to cyanidation as well as to amalgamation. Up to the introduction of flotation the best means for treating these ores involved a roasting operation followed by cyanidation, which is relatively expensive. In certain ores requiring roasting ahead of cyanidation the gold occurs as tellurides, in others in unknown form associated with the pyrite.

Flotation<sup>(22)</sup> has yielded high gold recoveries on these ores at a treatment cost which is lower than that necessitated by cyanidation and which is but a fraction of the cost of roasting followed by cyanidation. The grade of the concentrate has naturally varied with the ratio of gold to pyrite in the feed. Depending

upon local conditions, such as existence of and distance from smelter, smelter schedules, etc., the grade of concentrate differs which yields equal returns if shipped for smelting or if roasted and cyanided.

**Example 4<sup>(7)</sup>.**—A pyritic gold ore carrying gold, 0.48 oz. per ton; silver, 0.80 oz. per ton; and 10.95 per cent iron as marcasite, yielded satisfactory results by direct flotation if ground sufficiently fine. The results presented in Table 109 show the advantage of using xanthate.

TABLE 109.—METALLURGICAL RESULTS AND REAGENTS IN  
TREATMENT OF CANADIAN PYRITIC GOLD-SILVER ORE  
(After Godard.)

Test	Product	Weight, per cent	Assay		Recovery, per cent	
			Au, oz. per ton	Ag, oz. per ton	Au	Ag
A. . . . .	Concentrate	30.0	1.18	2.50	80.0	81.4
	Tailing	69.6	0.13	0.25	20.0	18.6
B. . . . .	Concentrate	30.1	1.60	2.70	93.2	89.2
	Tailing	69.9	0.05	0.14	6.8	10.8
C. . . . .	Concentrate	24.3	1.50	2.92	85.9	82.5
	Tailing	75.7	0.08	0.20	14.1	17.5

Test	Reagents	Quantity, lb. per ton	Added to
A. . . . .	Sodium sulfide	5.0	Ball mill
	Dupont flotation oil	0.40	Ball mill
	Pine oil No. 350	0.16	Ball mill
	Sulfuric acid	18.0	Ruth machine
	Pine oil (G.N.S. No. 5)	0.02	Ruth machine
	"Fumol" No. 6	0.02	Ruth machine
B. . . . .	Sodium carbonate	10.0	Ball mill
	Xanthate	0.80	Ruth machine
	Pine oil (G.N.S. No. 5)	0.06	Ruth machine
	Barrett's No. 4	0.40	Ball mill
C. . . . .	Pine oil No. 350	0.16	Ball mill
	Pine oil No. 350	0.16	Ruth machine
	Pine oil (G.N.S. No. 5)	0.08	Ruth machine
	Sulfuric acid	16.00	Ruth machine

**Use of Salt Water.**—An extensive series of experiments was conducted on Kalgoorlie ores<sup>(23)</sup> to determine whether flotation would be more economical than cyanidation. This investigation has spread over a span of 4 or 5 years and has disclosed that excellent results are obtained if flotation is conducted in saline solution. Even the older tests made with reagents which are now known not to be the best have yielded gold recoveries of the order of 92 to 95 per cent. Recent work has confirmed the belief that recoveries of 95 per cent or better can be expected. The following data are illustrative.

A gold ore (South Kalgurli ore) carrying gold, 0.7 oz. per ton (12.5 dwt.), associated with about 5 per cent pyrite, yielded a gold concentrate containing gold, 4 oz. per ton (75 dwt.) with a recovery of 94.8 per cent (average of nine roughing flotation operations carried out under slightly different conditions). Flotation was accomplished in a 2 per cent salt solution, the reagents consisting of kerosene (1 to 2.5 lb. per ton) and a mixture of eucalyptus oil, tar, and pyridine (1.4 to 3.6 lb. per ton).

It is stated by Winter and Moore that much cleaner concentrates were obtained through the use of salt or mine (salty) water than of fresh water. Indeed, the use of salt water practically doubled the grade of the concentrate. In view of the large quantity of oils used, it is possible that the beneficial effect of salt was simply to undo overoiling. Salt in the concentration of 2 per cent (on the water) is known to flocculate readily fine sus-

TABLE 110.—FLOTATION OF PYRITIC GOLD ORE  
(After Winter and Moore.)

Number of tests	Reagents					Average gold contents, dwt. per ton		Average recovery, per cent
	Salt, per cent on water	Potassium xanthate, lb per ton	Eucalyptus oil, lb per ton	Tar, lb per ton	Kerosene, lb. per ton	Concentrate	Tailing	
1	..	..	0.16	0.96	0.93	53.0	0.9	91.0
1	..	0.185	0.16	0.96	0.93	54.0	0.8	92.0
3	2	...	0.16	0.96	0.93	81.3	0.88	91.2
3	2	0.185	0.16	0.96	0.93	84.0	0.62	93.8
3	5	0.185	0.16	0.96	0.93	77.3	0.75	92.5

pended solids (effect of sea water on stream slime): its action on South Kalgurli ores may of course be related to this property.

The effect of floating in salt water and the slight beneficial action resulting from the use of xanthate as an additional collector are shown by Table 110.

**Importance of Adequate Grinding.**—Adequate grinding is of importance in the treatment by all-flotation of pyritic gold and silver ores (Table 111). Careful weighing of the increased

TABLE 111.—FLOTATION OF A COLORADO PYRITIC GOLD-SILVER ORE AFTER VARIOUS EXTENTS OF GRINDING\*

Metallurgical and economic data	Fineness of grinding, per cent —200 mesh					
	38	46	57	79	89	98
Tailing gold, oz. per ton.	0 066	0 050	0 037	0.032	0 022	0 015
Tailing silver, oz. per ton.	2 26	2.07	1.80	1.55	1 47	1 43
Concentrate gold, oz. per ton	5 76	6 11	5.73	4 67	4 18	4.63
Concentrate silver, oz. per ton	109 9	117 8	109 7	101 7	89 7	95.5
Gold recovery, per cent ..	85 0	88 5	91 5	92 1	94 4	96.6
Silver recovery, per cent..	75 6	77 7	81.0	83 6	84 4	86.2
Value of losses in tailing†	\$2 28	\$1 92	\$1 53	\$1 32	\$1.10	\$0 96
Approximate power and supply cost of grinding‡	\$0 18	0 27	0 36	0.54	0 72	1.08
Loss in tailing plus grinding cost	\$2 46	2 19	1 89	1 86	1 82	2.04

\* Reagents were as follows: amyl xanthate, 0.20 lb. per ton; pine oil, 0.12 lb. per ton; pH of tailing 7.6 ± 0.3

† Value which would approximately obtain (if concentrated) for silver at 55 cts. per oz.

‡ Power at 1.3 cts. per kilowatt-hour, balls and liners, 3 cts. per pound

recovery and increased cost resulting from finer grinding is necessary to determine the most economical milling conditions.

**Flotation of Cyanidation Tailings.**—The treatment of cyanidation tailings by flotation for the extraction of additional precious metals is gaining importance as the cost of flotation is decreasing and its effectiveness is increasing. Generally speaking, cyanidation does not extract the gold or silver occurring locked within pyrite particles and it achieves but a poor extraction on tellurides, selenides, and sulfides. It is precisely on those particles on which cyanide is relatively ineffective that flotation has the best opportunity for success: the two processes are supplementing each

other. The main difficulty in retreating cyanidation tailings by flotation is the low grade of the tailings. The following example illustrates what results may be obtained.

**Example 5.**—After dilution in a Dorr agitator a portion of the tailing of the cyanide plant at the Wright-Hargreaves mine in Ontario was floated in a MacIntosh cell having a capacity of one ton per hour. Reagents consisted essentially of soda ash, copper sulfate, coal-tar creosote, xanthate, and pine oil. Metallurgical results are presented in Table 112.

TABLE 112.—GOLD EXTRACTION FROM CYANIDATION TAILING OF WRIGHT-HARGREAVES MILL, ONTARIO (1927)

Date	Gold assay, oz. per ton			Gold recovery, per cent	Ratio of concentration
	Head (cyanidation tailing)	Concentrate	Tailing		
July 13	0 096	1 075	0 032	68 8	16 3
July 16	0 070	2 190	0 029	59 4	52 7
July 19	0 062	3 407	0 031	50 6	109
July 20	0 057	1 695	0 0235	59 6	49 8

In general the flotation of cyanide-plant tailings is more difficult than that of other low-grade products because of the inhibiting action of the residual cyanide and lime on the pyrite, and therefore on the gold. The effect of lime and cyanide can be overcome by washing the cyanide plant residues or by addition of a cyanicide such as copper sulfate and a lime-consuming agent such as soda ash.

**Rand Experiments.**—In view of the fact that the gold losses in cyanidation plants are largely in the coarser sand portions, a plant was built<sup>(1)</sup> to treat separately the sand and slime portions of a Rand ore pulp. The plant produced: (a) a slime pulp fed to the general cyanidation plant, (b) a sand flotation tailing fed to an auxiliary cyanidation plant, and (c) a sand flotation concentrate which was reground before feeding to a special cyaniding circuit.

By this method it was found possible to extract by flotation about two-thirds of the total gold, and at the same time to recover about 95 per cent of the pyrite. Cyanide sand residues were reduced to about 0.3 dwt. gold per ton (about 30 cts. per ton).

The flow-sheet is shown by Fig. 90. The pulp from the fine-grinding section was segregated by classifying cones ① into a slime going to the main cyanidation plant, and a sand going through mixing boxes ②, ③ to an eight-cell sub-aeration flotation machine ④ whose tailing went to the auxiliary sand cyanidation plant. The concentrate from ④ was thickened in a Dorr

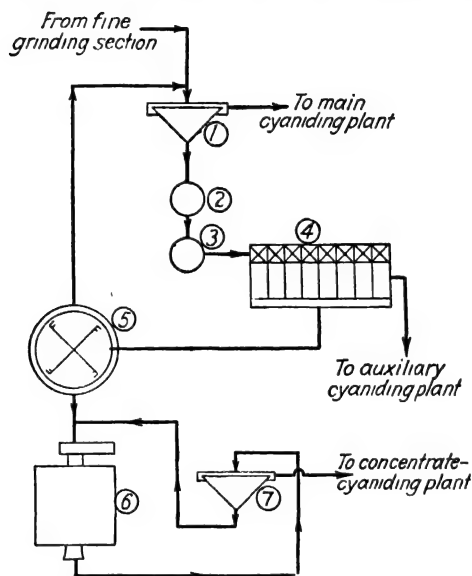


FIG. 90.—Combination flotation and cyaniding plant for the treatment of Rand pyritic gold ore.

thickener ⑤, ground with lime and cyanide in a tube mill ⑥ in closed circuit with a classifying cone ⑦, and cyanided in a separate plant.

The arrangement just described permits of concentrating the grinding action on a high-grade product (the flotation concentrate), instead of necessitating the grinding of a large bulk of very low grade material. For equivalent metallurgical results the grinding cost is therefore lessened.

#### TELLURIDE GOLD ORES

Telluride gold ores can be floated in cyanide solution yielding a high-grade gold concentrate of small bulk<sup>(19)(20)</sup>.

**Independence Mill.**—The Tippett process is in use at the Independence mill of the Portland Gold Mining Company,

Victor, Colo., in conjunction with gravity concentration and cyanidation (Fig. 91).

The pulp is coarsely ground ( $-30$  mesh) in cyanide solution in six 6- by 6-ft. ball mills ①, in closed circuit with Akins classifiers ②. The classifiers feed four eight-cell Ruth flotation machines ③ in parallel, whose tailing is concentrated further on 34 roughing

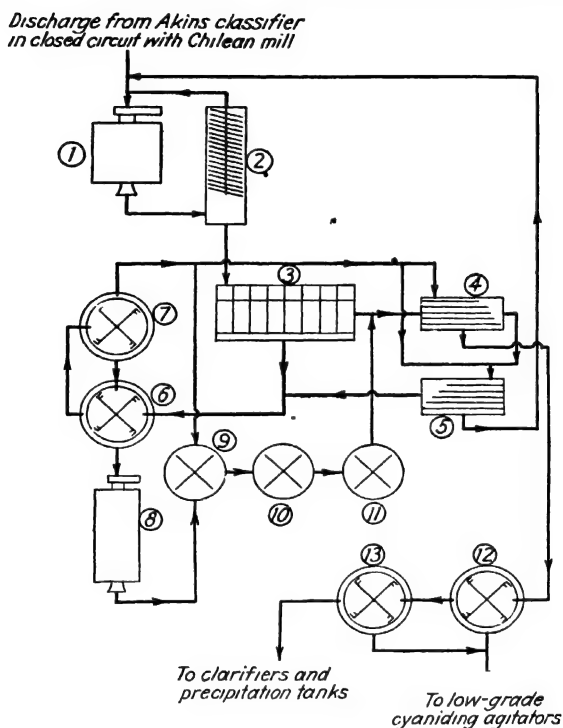


FIG. 91.—Grinding and concentrating divisions, Independence mill.

tables ④. The concentrate from the rougher tables is cleaned on 11 cleaning tables ⑤. The tailing from ⑤ is a middling product returned to ① for further grinding.

The concentrates from ③ and ⑤ are thickened in two thickeners in series ⑥ and ⑦ and ground in batches in a 5- by 14-ft. tube mill ⑧. The ground concentrates are cyanided for a long time (10 to 12 days) in agitators ⑨, ⑩, ⑪, arranged in series,

after which the pulp is returned to the first tables ④. The tailing from the roughing tables is segregated by Dorr thickeners ⑫, ⑬ into a feed for the low-grade cyanide agitators, and a solution to be clarified and treated for gold extraction.

At the Independence mill, flotation reagents consist of a mixture of nine-tenths fuel oil and one-tenth pine oil used to the extent of 0.2 to 0.4 lb. per ton.

### CARBONACEOUS GOLD ORES

It is known that carbonaceous material is undesirable in cyaniding gold ores: its presence results in low gold recovery and high cyanide consumption. Leaver and Woolf<sup>(12)</sup> have indicated that flotation can be applied to gold ores containing carbonaceous material (Mother Lode carbonaceous slime tailings).

Table 113 shows some of the results obtained from flotation with sodium amyl xanthate, 0.25 lb. per ton; cresylic acid, 0.05 to 0.125 lb. per ton; and pine oil, 0.05 to 0.10 lb. per ton.

TABLE 113.—FLOTATION OF CARBONACEOUS GOLD-ORE TAILINGS  
(After Leaver and Woolf.)

Origin of "slime"	Product	Gold assay, oz. per ton	Gold recovery, per cent
Argonaut.....	Feed	0.0665	
	Concentrate	1 62	69 0
	Cleaner tailing	0 40	18.2
	Rougher tailing	0 009	
Kennedy.....	Feed	0.099	
	Concentrate	2 05	85 3
	Cleaner tailing	0 28	7 2
	Rougher tailing	0 008	
Central Eureka.....	Feed	0 1375	
	Concentrate	1 345	82 5
	Cleaner tailing	0 055	4 0
	Rougher tailing	0 023	
Plymouth....	Feed	0 0433	
	Concentrate	0 555	72 7
	Cleaner tailing	0 040	11 1
	Rougher tailing	0 008	

### ARSENICAL AND ANTIMONIAL GOLD ORES

The flotation of gold ores in which the metal is closely associated with arsenopyrite presents no particular difficulties other



than those encountered in the treatment of pyritic gold ores, except the fact that arsenopyrite is generally less readily floated than pyrite.

**Collective Flotation.**—Table 114 presents results obtained on an arsenical gold ore (arsenopyrite) through the use of amyl xanthate, 0.25 lb. per ton, and cresylic acid, 0.10 lb. per ton, in a slightly acid pulp (pH 6.0). Cleaning of concentrate was done with addition of sodium silicate, 0.25 lb. per ton.

TABLE 114.—METALLURGICAL RESULTS OBTAINED ON ARSENICAL GOLD ORE

Product	Weight, per cent	Metal content		Recovery, per cent	
		Arsenic, per cent	Gold, oz. per ton	Arsenic	Gold
Feed		3 17	0 65		
Cleaner concentrate	7 1	39 40	7 70	88 1	84 4
Cleaner tailing	5 4	2 8	0 73	4 8	6 1
Rougher tailing	87 5	0 25	0 071	7.1	9.5

As in the case of the treatment of pyritic gold ores it is sometimes advisable to roast, then cyanide the arsenical concentrate rather than to ship it to a distant smelter. If antimony is present to a sufficient extent, it is likely to cause trouble during cyanidation. This has led to the desirability of separating antimony from arsenopyrite and gold by selective flotation.

**Gold-antimony Selective Flotation.**—Although gold is frequently associated with arsenopyrite, the stibnite occurring in the same ores is generally barren. Some success has been obtained in separating stibnite from arsenopyrite<sup>(3)</sup> (Table 115).

**Arsenic-antimony Selective Flotation.**—The separation of sulfide antimony from arsenic was also attempted by Canadian investigators<sup>(15)</sup>. They do not state whether the arsenic in the ore tested occurred as arsenopyrite or in an oxidized form, but from the ready flotation of the stibnite it may be inferred that the ore was a clean sulfide ore.

Study of the effect of various reagents led to the conclusion that best results were obtained in a circuit made acid with sulfuric acid (Table 116).

TABLE 115.—SELECTIVE FLOTATION OF AURIFEROUS STIBNITE ORES\*  
(After Clarke and Moore.)

Product	Weight, per cent	Metal content		Recovery, per cent	
		Gold, dwt. per ton	Antimony, per cent	Gold	Antimony
Antimony concentrate	6 1	16 0	7 99	9 3	62.6
Arsenic-gold concentrate	14 2	53 6	0 47	72 1	8.4
Tailing	79 7	2 45	0 29	18 6	29.0

\* Reagents for antimony flotation, eucalyptus oil, 0.5 lb. per ton; for gold flotation, potassium ethyl xanthate, 0.25 lb. per ton; selectivity index, antimony: gold 4.0.

TABLE 116.—SELECTIVE ANTIMONY-ARSENIC FLOTATION  
(After Parsons.)

Test number	Additional reagent used,* lb per ton	Product	Metal content		Recovery, per cent	
			Antimony, per cent	Arsenic, per cent	Antimony	Arsenic
1	None	{ Concentrate	64 20	0 28	86 7	9 6
		{ Middling	6 40	1 62	1 4	12.5
		{ Tailing	1 75	0 35	11.9	87.9
2	None	{ Concentrate	61 80	0 62	81 4	35 6
		{ Middling	4 50	1 04	13 4	13 5
		{ Tailing	0 88	0 27	5 2	50.9
3	Sodium carbonate, 4 0	{ Concentrate	62 70	1 00	83 6	40 0
		{ Middling	13 10	1 44	4 7	15 4
		{ Tailing	1 65	0 21	11 7	44.5
4	Lime, 4 0	No flotation				
5	Sulfuric acid, 10 0	{ Concentrate	63 40	0 31	95 6	16.4
		{ Middling	5 90	1 29	2 2	16 7
		{ Tailing	0 35	0 28	2 2	66 9

\* Besides pine oil and various collecting oils

**Pyrite-arsenopyrite Selective Flotation.**—A gold-copper ore body, newly discovered in Sweden, is composed principally of chalcopyrite, pyrite, and arsenopyrite. The gold occurs in the native condition in close association with chalcopyrite and

arsenopyrite, particularly the latter. The pyrite is barren. After considerable experimentation it was found best to make first an auriferous copper concentrate, then a barren pyritic concentrate, leaving most of the gold in the arsenical tailing.

### DRY SILVER ORES

By dry silver ores are meant sulfide-silver ores in which there is a small sulfide content in a highly siliceous gangue. Ores of this type are readily concentrated by flotation and yield high-grade concentrates. The silver occurs principally as argentite, freibergite (argentiferous tetrahedrite), the ruby silvers (proustite and pyrargyrite), and native.

The following instances are typical. A northwestern silver ore containing lead, 0.3 per cent; copper, 0.15 per cent; gold, 0.03 oz. per ton; and silver, 40.2 oz. per ton, principally as freibergite and ruby silver, was floated through the use of kerosene, 0.25 lb. per ton and coal tar, 0.25 lb. per ton (added to the grinding mill); amyl xanthate, 0.05 lb. per ton (added to the grinding mill); and cresylic acid, 0.05 lb. per ton (added to the flotation cell). The concentrate was cleaned without addition of reagents. Metallurgical results are presented in Table 117.

TABLE 117.—FLOTATION RESULTS ON A DRY SILVER ORE

Product	Metal content				Silver recovery, per cent
	Ag, oz. per ton	Au, oz. per ton	Pb, per cent	Cu, per cent	
Cleaner concentrate . . .	2073	1.35	14.6	8.1	93.8
Cleaner tailing . . .	21 5	....	..	..	1.9
Rougher tailing	1 82	....	..		4 3

A silver ore containing 21.9 oz. per ton (amalgamation tailing), chiefly as argentite and in the native state, was ground with soda ash, 5 lb. per ton and a coal-tar mixture, 0.75 lb. per ton. Flotation was accomplished with copper sulfate, 2.0 lb. per ton; xanthate, 0.1 lb. per ton; and pine oil, 0.17 lb. per ton. Metallurgical results are recorded in Table 118<sup>(14)</sup>.

### PLATINUM ORES

Flotation of platinum minerals, particularly of sperrylite and of sulfarsenides, has been reported<sup>(1)(16)(22a)</sup>.

TABLE 118.—FLOTATION RESULTS ON A DRY SILVER ORE  
(After Parsons.)

Product	Weight, per cent	Ag, oz. per ton	Recovery, per cent
Concentrate . . . . .	7 90	256.55	92 3
Tailing . . . . .	92.10	1.84	7 7
Screen Analysis of Tailing			
-65 + 100 . . . . .	3 88	17.59	34 1*
-100 + 150 . . . . .	12 10	2 94	18.0*
-150 + 200 . . . . .	8.92	1 88	8.5*
-200 . . . . .	75 10	1.06	39.4*

\* This recovery is expressed in percentage of the total tailing loss, which, as stated above, is 7 7 per cent of the silver in the feed

### MERCURY ORES

Mercury occurs generally as the sulfide, cinnabar. Occurrence of a mercurial tetrahedrite and of the metal in the native state has been noted. For practical purposes the problem is largely one of separating cinnabar from associated impurities, largely fine gangue and sulfur, and to make a clean tailing.

In the treatment of cinnabar ores Duschak<sup>(5)</sup> recommends the use of sub-aeration flotation cells. If sulfur is present it should

TABLE 119.—METALLURGICAL RESULTS OBTAINED ON SULFIDE  
MERCURY ORES\*  
(Courtesy, Minerals Separation North American Corporation.)

Test Num- ber	Product	Weight, per cent	Assay, Hg, per cent	Recovery, Hg, per cent	Selectivity index mercury: all gangue†
1	Feed		1 05		
	Concentrate	2 41	42 8	97.7	
	Cleaner tailing	8 23	0 18	1 4	59
	Rougher tailing	89 36	0 01	0 9	
2	Feed		11 65		
	Concentrate	15 7	73 2	98.6	
	Cleaner tailing	8 4	0 66	0 5	54
	Rougher tailing	75 9	0 14	0 9	

\* Reagents were the same in both cases, as follows: Roughing: Potassium ethyl xanthate, 0.8 lb per ton, steam-distilled pine oil, 0.2 lb per ton. coal-tar creosote, 0.6 lb. per ton. Cleaning: Potassium ethyl xanthate, 0.2 lb. per ton

† Discarding the cleaner tailing with the rougher tailing.

first be removed through the use of kerosene. Subsequently aerofloat or xanthate suitably collect the cinnabar.

In one instance a concentrate containing 62.8 per cent mercury and tailing containing 0.01 per cent mercury were produced from an ore containing 0.35 per cent mercury, indicating a mercury recovery of 97 per cent and a mercury-gangue selectivity index of about 125.

Native mercury and amalgam, such as are found in old gold and silver workings that had formerly been treated by amalgamation, are more difficult to float, perhaps because of the rounded shape of the droplets.

Table 119 presents some typical metallurgical results obtained on a cinnabar ore.

### MOLYBDENITE ORES

Molybdenite has long been known as one of the most floatable of minerals. This is in part due to its particularly non-polar character, to its non-oxidation, and to its micaceous habit.

In the flotation of molybdenite ores, a frother alone is generally sufficient: the reagent expense is very low. Sometimes a small amount of undissolved oil, such as kerosene, is useful to supply body to the froth. The usual collecting agents are distinctly to be avoided as they do not increase the recovery of molybdenum but serve to dilute the concentrate with pyrite, chalcopyrite, etc.

Molybdenum being rather valuable, molybdenite deposits are workable even if the metal content is low as judged by base-metal milling standards. Refining treatment requires the production of very high grade concentrates and special freedom from certain impurities. Exacting attention is therefore required of the operator, even though molybdenite is a highly floatable mineral. At the present time the market requires the concentrate to contain at least 85 per cent  $\text{MoS}_2$ ; copper is particularly undesirable.

The flaky character of molybdenite results in the flotation of many middling particles. This can be used to advantage to secure a low-grade primary concentrate featuring a high recovery. Subsequently, the primary concentrate can be ground further, and refloat. Thus a lower grinding cost is obtained than if complete liberation before concentration were attempted.

Timm and Parsons<sup>(18)</sup> classify molybdenite ores into several classes according to the size of the flakes and the relative abundance of pyrite and other sulfides. Other things being equal, a

lower grade feed, higher relative pyrite or pyrrhotite content, and finer flake make for a lower recovery or a concentrate of lower grade.

**Climax Mill**<sup>(4)(10)</sup>.—The mill of the Climax Molybdenum Company located at Climax, Colo., is treating about 1000 tons daily of a low-grade molybdenum ore containing some pyrite.

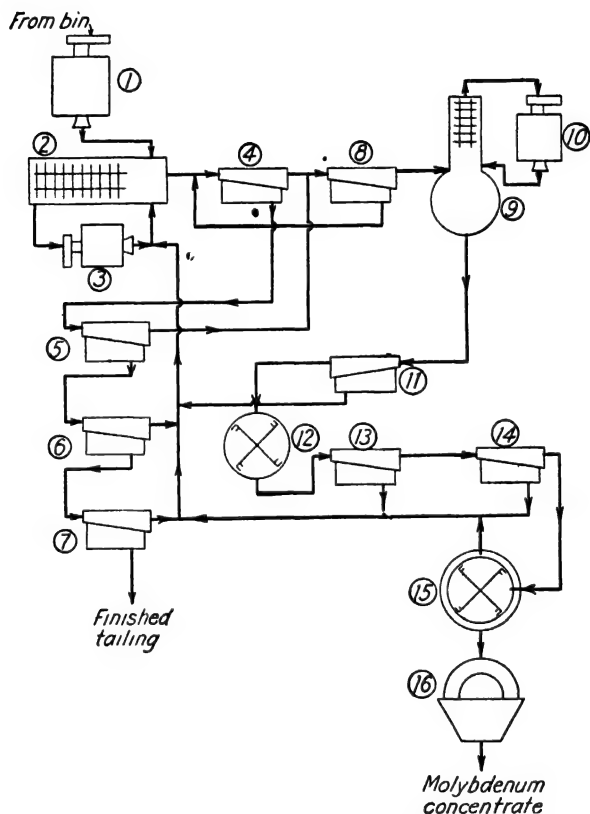


FIG. 92.—Grinding and flotation divisions, Climax mill.

The flow-sheet of the fine grinding and flotation divisions is shown in Fig. 92, from which it may be seen that the following are practiced: (a) two stages of fine grinding, one in open circuit and the other in closed circuit with Dorr classifiers; (b) one regrinding stage after roughing and cleaning flotation; (c) scavenging of the rougher tailing; (d) three cleaning steps of the

reground primary concentrate; and (e) dilution of the first cleaner concentrate to avoid over-frothing.

The ore is fed from the mill bin to three 6- by 6-ft. primary ball mills ①, which discharge into six Model C Dorr duplex classifiers ②, whose sand is ground further in two 6- by 10-ft. secondary ball mills ③.

The classifier overflow receives the reagents consisting of No. 100 Pensacola oil (a pine tar), 0.035 lb. per ton, and No. 5 G.N.S. steam-distilled pine oil, 0.094 lb. per ton, and is floated in two Callow rougher flotation machines ④. The tailing from these roughers goes to three Callow scavengers in series ⑤, ⑥, ⑦ making a finished tailing. The concentrate from ⑥ and ⑦ is returned to the classifiers ②. The rougher concentrate together with the concentrate from the first scavenger (15 per cent  $\text{MoS}_2$ ) goes to a Callow primary cleaner ⑧. This machine returns a middling to ④ and feeds a concentrate to one 8-ft. bowl classifier ⑨, set to overflow — 200 mesh material only. The bowl classifier is in closed circuit with a 4-ft. ball mill ⑩.

The bowl overflow goes to two secondary Callow cells in parallel ⑪, which make a 40 per cent concentrate and a tailing returned to the primary classifiers ②. The concentrate from ⑪ is diluted with water in conditioning tank ⑫ in order to prevent over-frothing in the recleaner ⑬ and re-recleaner ⑭ Callow cells. The tailings from these cells are returned to the primary classifiers ② and the concentrate from ⑭ is dewatered for shipment.

A 90 per cent recovery into an 87 per cent  $\text{MoS}_2$  concentrate is obtained with a ratio of concentration of 105:1 at an approximate cost of 70 cts. per ton. The selectivity index between molybdenite and the gangue is of the order of 80.





## CHAPTER XIII

### NON-METALLIC MINERALS

The term non-metallic as applied to minerals is used loosely to convey three different meanings. It refers to (a) minerals containing no metals, (b) minerals containing a metal or metals which are exploited for some other reason than their metal content, and (c) minerals possessing non-metallic luster. In addition to these substances, some metal oxides are considered in this chapter because of the similarity in flotative behavior to non-metallic minerals of class (c). According to the definition, the oxidized base-metal minerals discussed in Chap. XI belong here. However, convention is to consider them separately. In this book the term non-metallic is used reluctantly, yet there is no better name to describe collectively the miscellaneous minerals that are included in that term.

From a flotation standpoint non-metallic minerals fall into two great classes which are characterized by a very high and a very low natural floatability, respectively. Non-metallic substances included in the non-polar, highly floatable group are sulfur, graphite, bituminous coal, and anthracite. Non-metallic substances and oxides appearing in the polar, non-floatable group include oxides such as cassiterite and magnetite; carbonates such as calcite and rhodochrosite; sulfates such as barite; silicates such as quartz, feldspar, micas, garnets, and tourmalines; phosphates such as apatite; tungstates such as scheelite and ferberite; fluorides such as fluorite.

#### NON-POLAR NON-METALLIC MINERALS

Sulphur and graphite are non-polar elements possessing intense water-repelling properties. Coals, on the other hand, are extremely complex mixtures of oxyhydrocarbons in which deoxygenation and dehydrogenation have proceeded to a lesser or greater extent depending upon the temperature and pressure to which the carbonaceous matter was subjected.

The flotation of sulfur, graphite, and coals is facilitated by the low density of these substances, and in the case of graphite, by the flaky nature of the particles.

In contrast with native metals and the sulfides of lead, copper, silver, or iron, non-polar non-metallics are difficult to oxidize, and then they form gases:  $\text{SO}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . It is clear that their concentration by flotation is not so much a problem of accentuating or retaining the water-repelling properties of the mineral surfaces as it is a problem in preventing the flotation of associated gangue minerals.

To float sulfur, graphite, or coal it is often sufficient to add to the pulp a frother such as pine oil, the amount depending upon the fineness to which grinding has been conducted and upon the quantity of material to be recovered in the froth. The usual collecting agents, *viz.*, soaps and xanthates do not exercise any collecting function toward sulfur, graphite, or coal and are therefore simply wasted. Collecting oils, by their dispersion in fine drops, reduce the brittleness of a froth obtained by means of a frothing agent alone and are useful adjuncts particularly if the pulp is coarsely ground.

Reagents designed to inhibit gangue particles are desirable. Protective colloids such as glue, starch, casein, and sodium silicate are the commonest gangue-inhibiting substances. If used in moderation and with careful control, they reduce the flotation of fine gangue without affecting that of the minerals to be floated. Limitation of the amount of frother to the smallest quantity possible, and repetition of the cleaning operation, are helpful factors.

### SULFUR

Early experiments by Hyde<sup>(12)</sup> indicated that sulfur floats with great facility and that an 80 per cent concentrate with 80 per cent recovery can be made from an average ore. The reagents used included frothers, such as pine oils and cresylic acid; and other oils, such as coal-tar and wood-tar creosotes and kerosene. The main value of these collecting oils probably consisted in their forming droplets stabilizing the froth to some extent.

**Experimental Results.**—A synthetic mixture of sulfur and quartz was ground to pass a 35-mesh sieve and floated with terpeneol, 0.20 lb. per ton, and cleaned without additional reagents. Results are presented in Table 120.

TABLE 120.—FLOTATION OF SULFUR FROM QUARTZ-SULFUR MIXTURES

Product	Weight, per cent	Sulfur, per cent	Silica, per cent	Recovery, per cent	
				Sulfur	Quartz
Feed . . . . .	.....	30 0	70.0		
Cleaner concentrate . . . .	28 4	99 5	0.5	94.3	0.2
Cleaner tailing . . . . .	12.4	12 0	88.0	4.9	15.6
Rougher tailing . . . . .	59.2*	0.4	99 6	0.8	84.2
Sulfur to quartz selectivity index, roughing only . . . . .				25.6	
Sulfur to quartz selectivity index, cleaning only . . . . .				38.6	
Sulfur to quartz selectivity index, roughing and cleaning, discarding cleaner tailing . . . . .				90.8	

\* By difference.

Sherman reports the results of extensive tests<sup>(23)</sup> in floating sulfur from siliceous gangue in an ore from south-central Utah.

Table 121 illustrates the results obtained. It is claimed by Sherman that the best results were obtained with "Genasco"<sup>1</sup> in an alkaline rougher circuit and an acid cleaner circuit. Excel-

TABLE 121.—FLOTATION OF UTAH SULFUR ORE WITH MISCELLANEOUS REAGENTS  
(After Sherman.)

Reagent	Amount of reagent, lb. per ton	Grade of feed, sulfur, per cent	Grade of concentrate, sulfur, per cent	Sulfur recovery, per cent
Cresylic acid . . . . .	0 60	14.6	74 0	89 5
Pine oil (soda ash circuit) . . .	0.15	14 6	66.9	85.3
Gasoline . . . . .	0 60	14 6	65.9	91.5
Barrett No. 4 . . . . .	0.78	14 6	74 5	90 2
Crude turpentine . . . . .	0 15	14 6	65.3	90.1
T-T (lime circuit) . . . . .	0 12	14.6	82.0	84.0
Amyl alcohol (sulfuric acid circuit) . . . . .	0 17	32 5	83 7	88 4
Amyl alcohol (lime circuit) . .	0.25	32.5	79 8	88 7
Genasco (sulfuric acid cir- cuit) . . . . .	1 0	32.5	79.2	92.0

lent results were obtained also through the use of a frother only (amyl alcohol).

<sup>1</sup> An oil marketed by the General Asphalt Co.

Sherman states that limitation to concentration was set more by the fine texture of the ore (which precluded the making of a clean concentrate) than by any difficulty in floating the mineral.

The tests reported by Sherman were run on an ore containing pyrite as well as sulfur, the pyrite occurring to the extent of about one-tenth the sulfur by weight. Although no data are given, Sherman states that the use of lime would result in a satisfactory rejection of the pyrite.

A plant was erected in Utah to treat a sulfur ore similar to that on which the tests recorded in Table 121 were run. Results are said to be technically satisfactory but no operative details are available.

Variations in pH induce variations in grade of concentrate and in recovery<sup>(11)</sup>. For best results, operations should be conducted in the range, pH 7.5 to 8.0.<sup>4</sup>

**Refining Difficulties.**—Some difficulties in refining sulfur flotation concentrate are reported by H. L. Hazen<sup>(10)</sup>. The difficulties arose from the dispersing action caused by fine gangue and iron salts on the liquid sulfur. Hazen observed that liquid sulfur does not wet siliceous particles but that water does. By passing wet steam through the molten sulfur, gangue particles were given the opportunity of adhering to a layer of condensing water. The use of the two liquid phases and a gaseous phase condensing into a liquid phase (the wet steam) for preventing the siliceous material from polluting the sulfur is analogous to the bulk-oil flotation of early days with sulfur taking the place of water, water that of the bulk oil, and silicate particles that of sulfide particles.

**Marketing.**—From a practical standpoint it would seem that the field for the concentration of sulfur ores is limited. Among the factors entering into the problem the following may be mentioned:

1. Sulfur is a low-priced commodity.
2. Sulfur is available in huge quantities in relatively pure form (as in Louisiana and Texas where it is recovered by the Frasch process).
3. Sulfur is difficult to market because production is controlled by well-intrenched industrial organizations.
4. Sulfur melts at a relatively low temperature so that direct melting is an attractive alternative to flotation followed by melting.

## GRAPHITE

Due to its natural non-polar character, its low specific gravity and flakiness, graphite is one of the easiest minerals to float. Generally a small quantity of frother (0.05 to 0.2 lb. pine oil or cresylic acid per ton) is the only reagent needed. If there is much fine mica or other silicates present, sodium silicate or starch is a useful gangue-inhibiting agent. Little-soluble oils added in amount sufficient to exceed saturation (so as to occur as droplets) are useful froth-stabilizing adjuncts.

Table 122 presents the results obtained in floating at a coarse size a graphitic gneiss from the eastern United States. The

TABLE 122.—CONCENTRATION BY FLOTATION OF A GRAPHITIC GNEISS

Product	Carbon, per cent	Graphite recovery, per cent	Gangue rejection, per cent
Feed . . . . .	7.4		
Rougher tailing	0.8	10.1	94.9
Cleaner tailing	8.7	3.4	2.9
Cleaner concentrate	76.1	86.5	2.2

Selectivity index, graphite—all gangue:

Roughing cycle only	12.9
Roughing and cleaning together, discarding cleaner tailing.	16.9

reagents consisted of pine oil (0.2 lb. per ton) and of pine tar (0.1 lb. per ton) dissolved in the pine oil. On account of the relatively coarse aggregation of the minerals, grinding to 14 mesh was sufficient for liberation.

**Effects of Flakiness.**—Due to its flakiness and low specific gravity, graphite can be floated at a much coarser size than sulfides. Indeed, flakes measuring as much as 3 or 4 mm. in their two largest dimensions are floated easily if thin enough. The main difficulty in connection with the flotation of graphite is to achieve liberation of the minerals and at the same time to retain the flakes as coarse as possible, as the trade prefers coarse-flaked graphite and puts a substantial premium on it.

Cleaning and recleaning of graphite froths are necessary to eliminate the particles that should be rejected because these particles get tangled up in the froth between the flakes of graphite. This is well shown by data published by Timm and Carnochan<sup>(27)</sup> concerning the flotation of a somewhat weathered graphitic

gneiss composed of graphite, quartz, and a small amount of pyrite. The mineral was floated with coal oil (kerosene) and pine oil (amounts not stated) in a laboratory Janney machine and was cleaned three times, the carbon content of the four tailings being, in sequence: 0.30, 2.8, 13.8, and 26.5 per cent. Metallurgical data are presented in Table 123.

TABLE 123.—FLOTATION OF A CANADIAN GRAPHITE GNEISS  
(After Timm and Carnochan.)

Product	Weight, grams	Graphite content, per cent	Gangue content, per cent	Graphite recovery, per cent	Gangue recovery, per cent
Feed. . . . .	572*	16.0*	84.0*		
Re-re-cleaner concen- trate . . . . .	108	75.1	24.9*	88.6	5.6
Total middlings . . .	86	10.9	89.1*	10.2	15.9
Rougher tailing. . .	378	0.30	99.7*	1.2	78.5
Graphite—gangue selectivity index, roughing. . . . . 17.3					
Graphite—gangue selectivity index, roughing, cleaning, re-clean- ing and re-re-cleaning, calculating all middlings as rejected . . 11.5					

\* Calculated.

**Necessity and Limitations of Regrinding.**—In some instances association of graphite with the gangue is of such a nature as to allow the collection of a low-grade concentrate with good recovery after relatively coarse crushing. This impure concentrate is difficult to clean to a satisfactory extent without further grinding. Parsons<sup>(19)</sup> states that in one instance (Table 124) a high-grade concentrate could not be obtained without relatively fine grinding, and that retention of the graphite in flaky form could not be obtained together with liberation unless stage grinding were used. The increase in the graphite-gangue selectivity index from 14.7 to 17.8 and 24.4 with each successive regrinding is worthy of note as it shows the increased effectiveness of the separation with increased liberation.

**Screening and Tabling Flotation Concentrate.**—Screening of graphite flotation concentrates separates the tabular flakes from the relatively equidimensional gangue particles. Thus, a screening operation generally results in the segregation of the flotation concentrate into a coarse-flaked higher grade product and a small-flaked lower grade product (Table 125). In view

TABLE 124.—EFFECT OF REGRINDING AND REFLOATING ON A CANADIAN GRAPHITE ORE\*  
(After Parsons.)

Product	Weight, grams	Carbon, per cent	Graphite recovery, per cent	Gangue recovery, per cent
Feed. ....	988†	13.75		
Recleaner concentrate. . .	145	87.9	92.7	2.1
Recleaner tailing. ....	49	9.54	3.4	5.2
Cleaner tailing. ....	120	2.53	2.2	13.7
Rougher tailing. ....	674	0.35	1.7	79.0
Selectivity index after roughing. . . . . 14.7				
Selectivity index after roughing, grinding and cleaning, considering cleaner tailing as reject. . . . . 17.8				
Selectivity index after roughing, grinding, cleaning, regrinding and recleaning, considering cleaner and recleaner tailings as reject. . . . . 24.4				

\* Reagents for roughing were kerosene (1.0 lb. per ton) and pine oil (amount not stated).

† Calculated

TABLE 125.—EFFECT OF SCREENING ON GRADE OF GRAPHITE FLOTATION CONCENTRATES

Product	Carbon, per cent	Weight, per cent of total concentrate	Per cent of graphite in total concentrate
A. Concentrate 1(27)			
Total concentrate. . . . .	75.1		
+35-mesh fraction . . . . .	92.4	19.6	24.2
35/65-mesh fraction. . . . .	73.9	38.2	37.5
65/150-mesh fraction . . . . .	64.4	27.8	23.8
—150-mesh fraction . . . . .	75.8	14.4	14.5
B. Concentrate 2(20)			
Concentrate + 80-mesh fraction	61.9		
Concentrate — 80-mesh fraction	25.4		
C. Concentrate 3(2)			
Total concentrate. . . . .	84.0		
+ 90-mesh fraction. . . . .	89.4	78.9	84.2
90/150-mesh fraction. . . . .	78.5	8.6	8.1
—150-mesh fraction. . . . .	51.5	12.5	7.7

of the higher value placed by the graphite-consuming industry on the coarse-flaked material,<sup>(15)</sup> this segregation is often economically justified.

A similar separation to that obtained by screening can be obtained by tabling. The separation depends on the lesser specific gravity and flaky shape of the graphite particles. Typical results are recorded in Table 126.

TABLE 126.—EFFECT OF TABLING ON GRADE OF GRAPHITE FLOTATION CONCENTRATE

Product	Carbon, per cent	Graphite recovery, per cent
Flotation Concentrate 1(27)		
+100-mesh portion flotation concentrate	52.6	
Table concentrate from + 100-mesh flotation concentrate.....	85.3	93.0
Table reject from + 100-mesh flotation concentrate.....	10.3	
Flotation Concentrate 2(20)		
Whole flotation concentrate.....	33.7	
Table concentrate from flotation concentrate	42.3	98.9
Table reject from flotation concentrate. . .	1.8	

### COAL

**Effect of Low Specific Gravity.**—Even more than sulfur and graphite, coal is advantaged in flotation by its low specific gravity. This is well illustrated by the following. Consider a pulp consisting of 80 per cent water and 20 per cent coal sludge made up of equal parts by weight of bituminous coal of specific gravity 1.25 and slate of specific gravity 2.50. The average density of the pulp is 1.10; in other words, coal particles have to be buoyed to the extent of only 15 per cent of the volume of water that they displace in order to be floated. For comparison, it might be recalled that galena has to be buoyed to the extent of some 600 per cent of the volume of water that it displaces, or forty times as much as coal. In a quiescent medium it is possible to float coal particles eight times the diameter of the largest galena particles that may be floated. Correspondingly, under the vigorous agitation of flotation operation (obtained by either method of gas introduction), coal particles some eight times the maximum size of the galena particles floated in practice should be recoverable. Practically speaking, no galena coarser than 0.35 mm. is recovered. Accordingly, coal particles up to about 3 mm. should be satisfactorily recovered by flotation.



This is in agreement with the observations of Jones and Jones<sup>(14)</sup>.

**Impurities in Coal.**—The impurities occurring in coal are principally ash and sulfur. Ash occurs in three principal forms: (a) as coarse pieces of slate or other rock, (b) finely interbedded with coal as in "bone" coal, and (c) as inherent ash, very finely dispersed through the substance of the coal.

Slate is easily removed by gravity concentration from the coarse coal. Slate becomes concentrated in the finer portions of the coal, frequently constituting 40 to 60 per cent of the solid portion of colliery slush. The ash in bone coal is generally not removed by gravity concentration because liberation is not complete at the size at which gravity concentration is conducted but, if ground sufficiently, separation by flotation is possible. Inherent ash is so finely dispersed that it is practically unrejectable, even by flotation. A portion of it, however, is liberated and rejected in the operation of the Trent process (see below) for which extremely fine grinding is employed.

Sulfur occurs in three principal forms<sup>(26)</sup>: (a) as pyrite, (b) as calcium sulfate, and (c) as organic compounds<sup>(13)</sup>. If liberated, pyrite is readily eliminated by gravity concentration. But on account of the fine dispersion of pyrite in the seams and cracks of the coal, its liberation, and consequently its separation, are not as good as they might be. Calcium sulfate generally occurs finely disseminated, and the organic sulfur compounds are so intimately dispersed (molecularly?) throughout the coal that they cannot be separated by gravity concentration. Flotation can reject the calcium sulfate and pyrite but elimination of the organic sulfur has not been effected.

**Constitution of Coal.**—A great variety of substances go under the name of coal, from lignite and peat through bituminous coals (coking and non-coking) to semianthracite and anthracite. Coals are hydrocarbon substances of high molecular weight in which the H:C ratio is substantially less than in the usual substances of organic chemistry. From their essential constituents coals appear as non-polar substances which should be floated readily. Coals, however, contain considerable oxygen as C-O-H compounds and nitrogen as C-N-H, C-N-S-H, and C-O-N-H compounds, all of which contain polar groups. These heteropolar compounds, together with the ash inherently present in coal, are the naturally least floatable constituents. Oxygen

compounds and water decrease from peat to anthracite but ash increases. Maximum floatability probably occurs in some intermediate coals, perhaps in bituminous or sub-bituminous coals.

Stock-piled coal oxidizes and evaporates slowly, leaving a surface high in ash. This results in an increase of the polarity of particle surfaces and an inhibition of their floatability. Particles having fresh surfaces float better.

**Reagents for Coal Flotation.**—Although coals can be floated solely through the use of a frother, better results have been claimed to result from the joint addition of a frother and of an insoluble oil forming droplets that adhere to the surface of the particles. Coal-tar and wood-tar oils have been used in that connection, the usual quantity being 0.5 to 5 lb. per ton. Coal-tar and wood-tar oils have sufficient frothing qualities so that pine oils or cresylic acids can be dispensed with in some cases. For the rejection of, pyrite, lime with or without cyanide is effective (Table 127). Price<sup>(21)</sup> claims that the lower floata-

TABLE 127.—FLOTATION RESULTS ON A SYNTHETIC MIXTURE OF 50 PARTS CLEAN BITUMINOUS UTAH COAL, 40 PARTS SLATE, AND 10 PARTS PYRITE

Reagents, lb. per ton				Recovery, per cent*		
Pine oil	Coal-tar creosote	Lime	Cyanide	Coal	Slate	Pyrite
0.2	...	.	..	63	2	4
0.5	...	.	..	91	3	19
..	0 5	.	..	93	4	27
0.2	0 5	.	..	96	4	36
0.2	0 5	2 0	..	97	3	8
0 2	0 5	5 0	.	95	2	1
0 2	0 5	2 0	0 2	96	3	2

\* Estimated microscopically.

bility of the non-coking constituents of bituminous coals is lowered further by the addition of protective colloids such as tannin, starch, glue, and albumen.

**Typical Results.**—Tables 128 and 129 give the results of tests on the flotation of various English and American coals. In comparison with the results obtained in the flotation of sulfide ores, the selection obtained in coal-cleaning work appears poor.

TABLE 128.—FLOTATION OF ENGLISH COALS IN AGITATION-TYPE MACHINES  
(After Tupholme<sup>(29)</sup>.)

Kind of coal	Feed, ash, per cent		Concentrate		Tailing		(From calculated feed)		Selectivity index, coal ash
	Determined	Calculated	Weight, per cent	Ash, per cent	Weight, per cent	Ash, per cent	Coal recovery, per cent	Ash rejection, per cent	
Welsh coal.....	10.1	10.7	89.6	3.6	10.4	72.1	96.7	70	8.3
Derbyshire coal...	29.5	27.9	75.1	9.9	24.9	82.4	93.9	73	6.5
Coking coal.....	24.0	24.3	75.9	7.1	24.1	78.5	93.2	78	7.0
Coking coal.....	15.8	18.3	83.2	5.4	16.8	76.0	95.1	70	6.7
Non-coking coal..	21.8	27.5	69.6	7.3	30.2	74.4	89.3	82	6.2
Non-coking coal..	25.5	28.7	73.8	8.9	26.2	84.5	94.3	77	7.5
Slack.....	30.5	31.9	71.0	9.6	29.0	86.5	94.2	79	7.8
Silt.....	45.2	39.1	59.0	12.5	40.5	82.8	88.1	80	6.7
Washery dump...	40.3	39.8	53.0	7.9	47.0	75.8	80.7	89.5	6.0
Washery dump ..	75.0	76.5	16.2	14.0	83.8	88.5	59.0	97	6.8

This in itself is a confirmation of the imperfect liberation at which segregation is attempted.

**Technical and Economic Limitations.**—Application of flotation to coal washing has made almost no headway in the United States although there are British, Continental, and Japanese washeries using flotation. The American reticence to using flotation for coal concentration arises from several causes which are economic rather than technical.

Among the technical factors limiting the use of flotation for the beneficiation of coals must be mentioned the unsatisfactory liberation of coal from the associated ash resulting even from relatively fine grinding, and our general ignorance of the chemical and physical constitution of the complex oxynitrohydrocarbons of coals.

The economic factors are dominated by the fact that coal is a low-priced commodity which cannot be handled except by a very economical process. In most cases this precludes fine grinding. The stumbling block seems to be the low relative value that is placed on the fine sizes and the lack of demand for the briquettes which could be made from flotation concentrate. In Europe, coal briquettes have been used for some time, and coal has a relatively higher value at the mine on account of the

TABLE 129.—FLOTATION OF NORTHWESTERN AMERICAN COALS IN AGITATION-TYPE MACHINES  
(After Ralston (22).)

Kind of coal	Reagents, lb per ton	Feed, ash, per cent		Concentrate		Tailing		Fuel recovery, per cent	Ash recovery, per cent	Selectivity index, coal : ash
		Determined	Calculated	Weight, per cent	Ash, per cent	Weight, per cent	Ash, per cent			
Low-grade sub-bituminous	Kerosene, 4.8 Pine oil, 1.2	15.3	15.6	79.8	13.1	20.2	25.3	82.1	33	1.5
Low-grade sub-bituminous	Kerosene, 5.0 Hardwood creosote, 1.0	15.3	16.7	95.5	14.4	4.5	66.2	98.2	17.5	3.4
Good sub-bituminous	Crude pine creosote, 4.0	20.8	20.8	75.0	15.5	25.0	36.8	80.0	44	1.8
Good sub-bituminous	Crude pine creosote, 2.0	20.8	20.8	91.8	16.5	8.2	68.5	96.3	27	3.1
Bituminous, non-coking	Kerosene, 4.0	26.5	26.4	82.3	18.4	17.7	63.9	91.3	43	2.8
Bituminous, non-coking	Pine oil, 1.5	26.5	26.7	82.6	19.7	17.4	60.0	90.5	39	2.5
Bituminous, coking	X-cake and xyldin, 3.0	24.7	24.9	89.9	18.8	10.1	79.2	97.2	32	4.0
Semianthracite	Pine oil, 2.5	13.7	13.5	96.5	11.5	3.5	67.2	98.7	17.5	4.0
Semianthracite	Kerosene, 2.0	13.7	13.7	92.6	10.0	7.4	59.9	96.6	32.5	3.7

generally lower grade of the coal seams and of the shorter distance to the consumer. A better opportunity exists therefore in Europe to apply flotation as a last salvaging step in coal washing. Even assuming that briquettes made from coal flotation concentrates could be sold, the dewatering and drying of the concentrates would entail such a large cost (several times the cost of flotation itself) as to substantially reduce the margin of profit resulting from the recovery of an additional quantity of coal from colliery fines.

When a willingness develops to pay a premium for fine-sized, relatively ash-free coal over the price of coarse, high-ash coal, the technique of production will be available.

**Trent Process.**—The Trent process<sup>(28)</sup> is related to flotation although it does not involve a floating operation. Cleaning coal by the Trent process consists in agitating finely ground ashy coal with water and a substantial amount of oil; then in separating the oil-coal aggregates or granules from the water which retains the ashy particles. Trent recommends the use of fuel oil, crude oil, benzol, or gasoline up to one-half the weight of the carbonaceous content of the raw coal. After some agitation, the coal particles and the oil form aggregates which can be separated from the water by filtering or simple draining at the end of the granulating period. Gentle agitation is preferred to vigorous agitation as it allows the formation of coarser granules and results in a cleaner coal product.

The Trent process is related to the early bulk-oil flotation processes in which levitation of the mineral particles was derived from the buoyancy of the oil rather than of the air. It differs from them in that the oil is not used to buoy the coal particles but only to separate them from the ash in the form of relatively coarse granules having a specific gravity but slightly larger than water. The parent invention to which the Trent process is related is disclosed in several patents issued to Cattermole in 1904<sup>(3)</sup>.

Taggart says<sup>(25)</sup>

the physical phenomena underlying granulation are the same as those acting in agitation-froth flotation, *viz.*: preferential coating of the mineral particles with oil followed by gas precipitation on the oiled particles [*but see Chap. VI*]. Subsequently excess oil meets and spreads on the mineral-coated bubbles, and when the oil coating becomes sufficiently thick, most of it, together with the mineral, which has been displaced to

the oil-water interface, slips off the bubble like a sheath. This sheath is relatively viscous by reason of the solid coating and rolls up, under the swirling action of the pulp, into the characteristic granule.

The viscosity of the oil used in granulating affects the results: the more viscous the oil, the higher the recovery and the lower the ash rejection (Table 130). It is not definitely known what effect the exact chemical composition of the oil and the pH of the

TABLE 130.—PERFORMANCE OF TRENT PROCESS ON COAL FROM  
THE NORTHWESTERN UNITED STATES, GROUND TO PASS A  
300-MESH SIEVE  
(After Ralston<sup>(22)</sup>.)

Oil	Relative viscosity	Feed, ash, per cent	Concentrates (granules) ash, per cent	Coal recovery, per cent	Ash rejection,* per cent	Selectivity index
Gasoline . . . .	0.95	25.9	8 0	91 8	77	6.1
Crude benzol	0.97	25.9	9 4	90.9	73	5.2
Kerosene	1 0	25.9	9.5	93.1	72	5.9
Stove oil (30°)	1 3	25.9	9 6	95 9	71	7.5
Crude oil (25°)	5 0	25 9	11 8	96 7	63	7.1
Residuum (18°)	50 0	25.9	12 2	97 4	61	7.6
Asphaltum (10°). . .	Very high	25 9	13 5	98 2	56	8.3

\* Calculated from feed and concentrate ash content and from the coal recovery in the granules.

pulp have on the performance of the process, other than that they have some effect. Taggart states that a small amount of oleic acid greatly improves the operation of the Trent process.

Comparison of the Trent process with flotation (Table 131) is in favor of the Trent process which yields a higher coal recovery, a higher ash rejection, and higher selectivity index than flotation when the pulp is ground to the same fineness. Furthermore, the Trent process is suited to the treatment of finer pulps than flotation, and this finer grinding results in more complete liberation of the coal from the ash and therefore in more effective cleaning. Ralston concludes as follows concerning the Trent process and flotation as applied to coal cleaning<sup>(22)</sup>:

1. Froth flotation and the Trent process, when applied to the cleaning of various coals ground to pass a 65-mesh sieve for the purpose of preparing a low-ash fuel, gave very similar results under conditions which

TABLE 131.—COMPARISON OF TRENT PROCESS WITH FLOTATION ON  
PACIFIC NORTHWEST COALS  
(After *Ralston*(22).)

A. Coal ground to pass a 65-mesh screen								
Trent process					Flotation			
Type of coal	Granule concentrate, per cent ash	Coal re- covery, per cent	Ash re- jection, per cent	Selec- tivity index	Concen- trate, per cent ash	Coal re- covery, per cent	Ash re- jection, per cent	Selec- tivity index
Low-grade sub-bituminous	13.5	99.0	14	4.0	13.8	90.4	20	1.6
Good sub-bituminous	13.5	98.0	42	6.0	15.5	80.0	44	1.8
Bituminous, non-coking....	16.3	96.0	48	4.7	18.4	90.0	43	2.6
Bituminous, coking.....	18.0	98.5	34	5.8	18.8	96.0	32	3.3
Semianthracite...	10.8	99.0	26	5.8	10.7	97.0	27	3.4
			Average	5.2			Average	2.5
B. Coal ground to pass a 300-mesh screen								
Type of coal	Granule concentrate, per cent ash	Coal re- covery, per cent	Ash re- jection, per cent	Selec- tivity index				
Low-grade sub-bituminous	9.0	99.5	41	13.0				
Good sub-bituminous	10.6	98.0	56	7.9				
Bituminous non-coking.	12.2	98.0	62	8.9				
Bituminous coking.	15.8	99.5	43	12.3				
Semianthracite	7.7	99.5	48	13.6				
			Average	10.9				

were most favorable to the froth-flotation work and somewhat unfavorable to the Trent work.

2. Under these conditions the grades of concentrate made by the two processes were almost identical for all kinds of coals tested, with a slight advantage in favor of the Trent process when heavy oils were used, and a pronounced advantage when light oils were used.

3. The extractions of combustible matter are higher in the Trent process, the differences being slight for semianthracite and coking bituminous, but up to 5 or 10 per cent for the lower grades of coal.

4. The Trent process carries the bony coal into the "clean" coal product whereas it is possible by froth flotation to carry the cleanest coal into a first concentrate and the bony coal can then be taken off in a second concentrate, which can be segregated if desired. For this reason the froth-flotation process is the more flexible of the two.

5. The Trent process has been operated successfully on material that has been ground to pass a 300-mesh screen, whereas froth flotation has been successfully used to date only on material ground to pass a 65-mesh screen, although good flotation work can be done on all sizes of coal but the "slime."

6. The question of disposal of the concentrate is most important in considering the value of a process and though each process is now in use the field of usefulness of the two products is still largely to be determined; it is possible that the two processes could even be used to advantage to supplement each other.

7. As at present developed froth flotation is competing with the coal-washing table for cleaning fine granular portions of coal, whereas the Trent process is in use for the more finely divided and slimed coal.

### POLAR NON-METALLIC MINERALS

In 1920 flotation of polar non-metallic minerals was hardly considered possible. Since that time it has been found possible to float almost any mineral of this wide group of substances, but selection of one mineral from another has been accomplished in a few instances only. The prospects for expanding success are good.

Generally speaking, the only way known today to float polar non-metallic minerals is to form insoluble soaps at their surface by reaction between the surface of the minerals and dissolved soaps or fatty acids, or between ions or molecules of an activating agent adsorbed at the surface of the mineral, and dissolved soaps or fatty acids. In contrast to the requirements for the flotation of non-polar non-metallics, collectors are the most necessary and important of the reagents. Frothers are needed, but as soaps possess foaming properties it is frequently unnecessary to add a separate reagent for frothing. Indeed, in many cases the soap or fatty acid used is too active as a frother.

Of the many fatty acids and soaps known to organic chemistry, the fatty acids of the paraffin series ( $C_nH_{2n+1}COOH$ ) and oleic acid ( $C_{17}H_{33}COOH$ ) which belongs to the olefin series ( $C_nH_{2n-1}COOH$ ) have alone been studied. Oleic acid, and

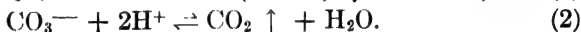
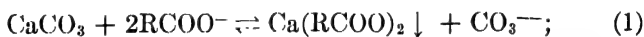


palmitic acid ( $C_{16}H_{33}COOH$ ) are the only fatty acids that have been used in practice. The reason is that some of the most useful fatty acids are still considered as rare substances since there is no demand for them and therefore no immediate supply. When demand justifies, a number of these fatty acids may become available at a price in the range of 15 to 50 cts. per pound. Of fatty acids belonging to other series than the paraffin and olefin series nothing is known.

In most non-metallic ores, the substances to be rejected are calcium carbonate and silica. Lime often occurs as calcite—although it may be microcrystalline and more or less impure, as in limestone. Silica occurs as quartz and in the form of silicates, *e.g.*, feldspars, micas, pyroxenes, and amphiboles.

### CALCITE,

Calcite is floated readily by fatty acids of the paraffin series<sup>(3a)</sup> (Fig. 93). The reaction chain is



**Importance of pH.**—The great importance of pH changes on the flotation of calcite (and also on the flotation of most polar

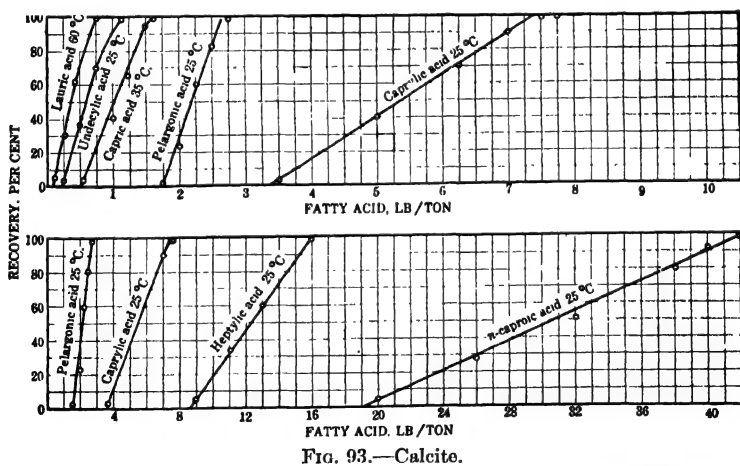


FIG. 93.—Calcite.  
Flotation of 65/100-mesh particles with saturated fatty acids.

non-metallics) is suggested by the above equations. As the pulp is made more alkaline, the hydrogen-ion concentration decreases in accordance with:

$$[H^+] \times [OH^-] = 10^{-14}. \quad (3)$$

Thus, for every increase in pH of one unit the hydrogen-ion concentration is decreased ten-fold and the carbonate-ion concentration must be increased one hundred-fold for reaction (2) to proceed to the right. This in turn necessitates an increase of the fatty anion if reaction (1) is to proceed to the right. It is apparent, therefore, that too great an alkalinity will inhibit flotation

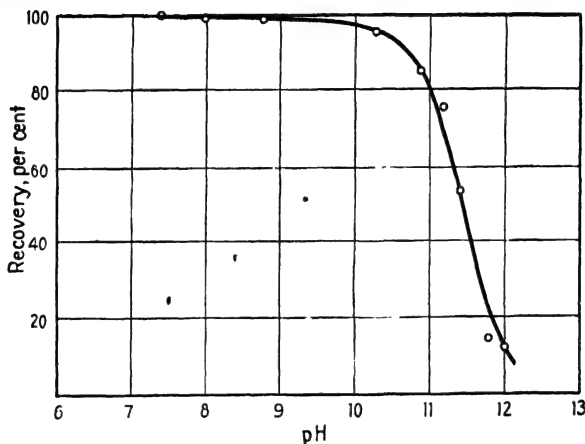


FIG. 94.—Calcite.

Effect of pH on the recovery of 100/600-mesh particles using oleic acid, 0.50 lb. per ton, and variable amounts of NaOH.

of calcite with soap. Too great an acidity reduces the fatty anion in accordance with the dissociation constant of the fatty acid,

$$\frac{[\text{H}^+][\text{RCOO}^-]}{[\text{dissolved RCOOH}]} = \text{constant}; \quad (4)$$

and prevents the reaction stated by (2) from proceeding to the right. In the case of calcite, acid pulps are incapable of stable existence because of the decomposition of calcite by acid,

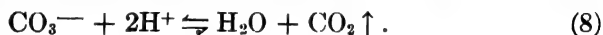
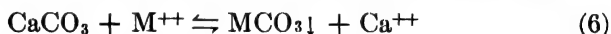


Even if the pulp is made momentarily acid, the pH quickly reverts to neutrality or even to slight alkalinity, in the immediate vicinity of every calcite particle. Reduction in the effectiveness of fatty acids by the use of substantially acid pulps therefore cannot take place with calcite.

An instance of the effect of pH on the recovery of calcite by oleic acid is presented in Fig. 94.

**Activation of Calcite.**—No activating agents are necessary to increase the floatability of calcite with the higher fatty acids.

With lower fatty acids, such as heptylic acid ( $C_7H_{15}COOH$ ), copper and lead salts help float the mineral with less collector: apparently the activating salt reacts first with the mineral to form a lead or copper carbonate coating which, in turn, reacts with the fatty-acid anions to form a coating of lead or copper soap. Because this lead or copper soap is less soluble than the calcium soap that would otherwise form, adherence of the filmed particles to bubbles results at a lower concentration of the fatty acid than would obtain in the absence of lead or copper ions:



**Inhibition of Calcite.**—Just as some salts capable of forming insoluble soaps activate calcite, certain other salts which form colloidal hydroxides result in depression of calcite. Chromium nitrate is typical.

### QUARTZ

**Activation of Quartz.**—Early reports<sup>(8b)</sup> to the contrary, pure quartz cannot be floated materially with soaps. It is easily activated by a great number of salts, particularly those of ferric, cupric, lead, zinc, barium, and calcium ions. Following such an activation, quartz can be floated readily. The exact form of the activation is unknown, but it is known analytically that the cations of the activating salts are abstracted by quartz. Quartz that has a coating of metal ions in turn abstracts fatty ions from solution and is floated thereby. The actual floating agent is probably a metal soap. It is of interest to note that the metal salts which do not activate quartz are (a) those that do not form insoluble soaps and (b) those that form colloidal hydroxides in strongly acid solutions. Alkali-metal and chromic salts are typical of these exceptions.

Flotation of quartz without apparent activation was obtained in metallic flotation machines, and led to the premature conclusion that quartz is floated by soaps without activation. Repetition of the experiments in celluloid cells, in the absence of activators added deliberately, resulted in much reduced flotation. Some flotation, however, was observed over a narrow pH range near neutrality. This is believed to have arisen from activation by the calcium ions of the tap water in which the

mineral had been washed before flotation. If quartz is washed in distilled water prior to flotation, and then floated in distilled water modified by hydrochloric acid or sodium hydroxide, it is practically uncollectable by soaps.

Changes in pH affect most markedly the flotation of activated quartz (Fig. 95).

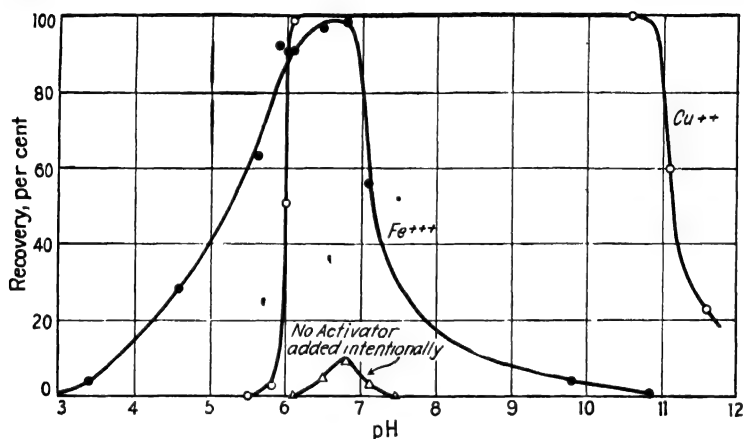


FIG. 95.—Activated quartz.

Effect of pH on the recovery of 100/600-mesh particles activated by ferric chloride, 1.00 lb. per ton, or cupric nitrate, 1.00 lb. per ton, using sodium oleate, 0.20 lb. per ton, terpeneol, 0.20 lb. per ton, and NaOH or HCl to suit.

**Inhibition of Quartz.**—In most cases it is desired to prevent quartz from floating. Generally this is not difficult to achieve. In many instances quartz does not float with the other minerals from which it is to be rejected so that a collector and frother are sufficient to bring about the separation. If quartz displays a marked tendency to float with soaps and fatty acids (perhaps the result of natural activation), inhibition can be obtained by using sodium silicate. The exact nature of the inhibiting action of sodium silicate on quartz is unknown. It may be a somewhat selective protecting action resulting from the colloidal character of the silicic acid formed by hydrolysis of the sodium silicate; it may also be caused by a competition for the activating cations available in the system set up by the large surface of the silicic acid micelles derived from the sodium silicate.

Sodium carbonate and sodium phosphate have inhibiting qualities for silica, which in attenuated form resemble those of sodium silicate. Their effect can hardly be ascribed to the

influence they exert on the pH, because the same effects do not necessarily obtain if the pH is adjusted to the same value with sodium hydroxide. Rather, the effect appears related to the  $\text{CO}_3^{--}$ ,  $\text{HCO}_3^-$ , or  $\text{HPO}_4^{--}$  anions.

It is likely that the commonest cations activating quartz naturally are the alkaline-earth cations, particularly calcium ion, which on account of the widespread occurrence of lime and lime compounds in nature exists in nearly all ores and minerals.

#### CONCENTRATION OF CARBONATE NON-METALLICS

Separation of carbonates from quartz is obtainable by the use of oleic acid (or sodium oleate), a frother, and sodium silicate.

**Separation of Calcite from Quartz.**—The possibility of separating limestone from silica was suggested a few years ago<sup>(17)</sup>. Table 132 shows that marked increase in the selection of calcite from quartz results from the use of a small amount of sodium silicate (selectivity index changed from 6.0 to 10.9), but that no corresponding increase results from the use of gum arabic (selectivity index changed non-significantly from 6.0 to 5.6).

TABLE 132.—SELECTIVE FLOTATION OF CALCITE FROM QUARTZ  
(Synthetic Mixtures of Pure, Deslimed Minerals.)

Test number	Reagents, lb. per ton					Calcite recovery, per cent	Quartz rejection, per cent	Selectivity index, calcite: quartz
	Terpinacol	Sodium oleate	Sodium silicate	Gum arabic	Copper sulfate			
1	0 10	0 10	....	....	....	95	67	6 1
2	0 10	0 20	....	....	....	99	25	5 8
3	0 10	0 20	0 05	....	....	97	78	10 7
4	0 10	0 20	0 10	....	....	92	92	11 5
5	0 10	0 20	0 20	....	....	53	99	10 6
6	0 10	0 20	....	0 03	....	85	74	4.1
7	0 10	0 20	....	0 04	....	82	91	6 9
8	0 10	0 20	....	0 05	....	64	96	6 6
9	0 10	0 20	....	0 08	....	8	99 5	4 5
10	0 10	0 20	....	....	0 20	95	8	1 3
11	0.10	0 20	0 10	....	0 20	94	14	1 6
12	0 10	0 20	0 20	....	0 20	92	57	3 7
13	0.10	0 20	0.30	....	0.20	80	86	5 0

It is also clear that activating salts such as cupric salts are objectionable, in that they obliterate the natural differences

in floatability between calcite and quartz. Their effect can be overcome in part through the use of sodium silicate.

The separation of malachite, cerussite, and smithsonite from siliceous minerals (Chap. XI) through the use of fatty acids is based on the same principles as the separation of calcite from quartz.

**Beneficiation of Rhodochrosite Ores.**—The flotation of manganese ores in which the metal occurs as the carbonate has assumed commercial importance. The flotative properties of rhodochrosite<sup>(8c)</sup> being similar to those of calcite, it would naturally be expected that its separation from quartz and silicates should follow the same methods.

Variations in pH affect materially the separation of rhodochrosite from quartz (Table 133 and Fig. 96). Optimum selection is obtained in the pH range of 7.5 to 9.0.

TABLE 133.—EFFECT OF pH ON RHODOCHROSITE-QUARTZ SEPARATION IN MIXTURES OF PURE DESLIMED MINERALS (−100 + 600 MESH) (40 PARTS RHODOCHROSITE, 60 PARTS QUARTZ)

Test number	Reagents, lb. per ton				pH	Rhodochrosite recovery, per cent	Quartz rejection, per cent	Selectivity index
	Sodium oleate	Terpineol	Sodium hydroxide	Hydrochloric acid				
1	0 10	0 10	.	2 5	5 5	40	90	2.4
2	0 10	0 10	.	0 5	6 7	69	81	3.1
3	0 10	0 10	.	0 2	6 7	88	59	3.3
4	0 10	0 10	.	0.05	7 2	92	53	4.2
5	0 10	0 10	.	.	7 6	91	61	4.0
6	0 10	0 10	0 07	..	7.8	95	66	6.1
7	0 10	0 10	0 12	.	8 3	97	71	8.8
8	0 10	0 10	0 20	.	9 6	95	51	4 4
9	0 10	0 10	1 0	..	10 8	95	20	2.2
10	0 10	0 10	3 0	..	11 5	89	13	1 1

Improved separation results from the additional use of sodium silicate (Table 134). The beneficial effect of sodium silicate can be ascribed in part to the change in pH resulting from its use, and in part to the silicate radical itself.

Application of flotation to manganese carbonate ores has been successful in the laboratory<sup>(30)</sup> as well as in pilot plants. A plant is said to be equipped to treat a large daily tonnage of manganese

carbonate ore in the Butte District, Mont. In the Butte ores rhodochrosite is associated with sulfides in varying amount and particularly with sphalerite and pyrite. These sulfides are a

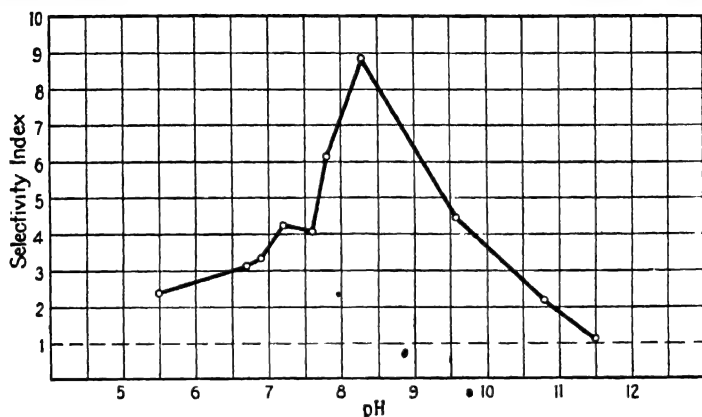


FIG. 96.—Rhodochrosite-quartz separation.  
Effect of pH on the selectivity index. (1:4 mixtures; 100/600 mesh.)

valuable by-product if segregated from the rhodochrosite but an objectionable impurity in the manganese concentrate. Accordingly they are first removed from the pulp as a collective sulfide concentrate. This concentrate may be obtained by the addition of xanthates, pine oil, and copper sulfate. Following the production of a collective sulfide concentrate, the pulp may be conditioned with soap and waterglass and floated for manganese extraction.

TABLE 134.—EFFECT OF ADDITION OF SODIUM SILICATE ON  
RHODOCHROSITE-QUARTZ SEPARATION IN MIXTURES OF PURE  
DESLIMED MINERALS (−100 + 600 MESH) (40 PARTS  
RHODOCHROSITE, 60 PARTS QUARTZ)

Test number	Reagents, lb. per ton			pH	Rhodochrosite recovery, per cent	Quartz rejection, per cent	Selectivity index
	Sodium oleate	Terpincol	Sodium silicate				
1	0 10	0 10	.	7.6	91	61	4 0
2	0.10	0.10	0 05	8.1	94	81	8 1
3	0 10	0.10	0 075	8.3	91	91	10.1
4	0 10	0 10	0 10	8.4	88	96	13.1
5	0.10	0.10	0.20	8 6	63	98.5	10 6

Figure 97 is a proposed\* flow-sheet in which ① and ④ are conditioning tanks for sulfide and rhodochrosite flotation; ② and ③ are the rougher-cleaner-recleaner for sulfide flotation and ⑤ the rougher-cleaner-recleaner for manganese flotation.

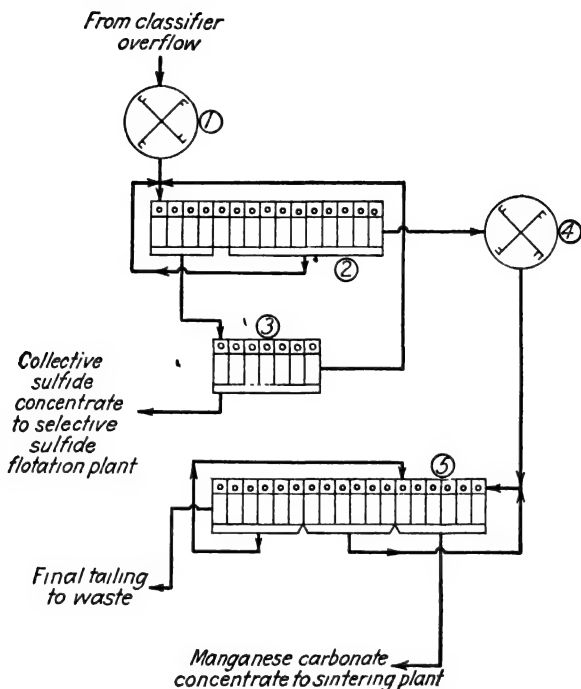


FIG. 97.—Proposed flow sheet for the flotation of a sulfide-bearing rhodochrosite

### SEPARATION OF CARBONATES FROM EACH OTHER

Individually, different carbonates display different reactions to flotation with soaps. In spite of this it has not been found possible to separate them by means of soaps, as the flotative behavior of a mixture of free carbonates of two or more kinds is intermediate between that of the carbonates tested singly: flotation of such a mineral mixture results, not in successive flotation of the two mineral species, but in their simultaneous flotation. For instance, calcite and malachite behave differently when floated separately with heptylic acid, malachite requiring much less reagent for a given recovery to result; but mixtures of calcite and malachite behave as though the particles



of the two minerals had identical surfaces. Since this is the case, the difference in behavior of malachite and calcite when exposed to amyl xanthate appears particularly unusual. A cause is perhaps to be sought in the facts that intermediate fatty acids do not float the carbonates except at a pH such that solution of the mineral by hydrogen ion is proceeding to some extent, whereas amyl xanthate floats malachite best at a pH at which solution of the minerals by hydrogen ion is much reduced. Since calcite abstracts copper ion from solution, the pH necessary for flotation with fatty acids may result in the production of identical surfaces on particles of the two minerals, although the pH necessary for flotation with xanthates may not. Another cause for the lack of discrimination between malachite and calcite by heptylic acid, and of the splendid separation achieved by xanthates, may be the small ratio in the solubilities of calcium heptylate and copper heptylate as compared to the ratio in solubilities of calcium amyl xanthate and copper amyl xanthate.

Reasoning by analogy to the malachite-calcite case, it appears that, as a working hypothesis, the prospects for separation of one carbonate from another are good only if (a) the collector to be used forms a much less soluble compound with the metal in one carbonate than with that in the other, and (b) the separation can proceed at a pH that involves no substantial solution of either carbonate. So far success is lacking for separations other than those involving lead, copper, and zinc carbonates.

#### FLUORITE

Like calcite, fluorite (fluorspar) is easily floated with soaps. The greater solubility of fluorite as compared with calcite causes the reaction



to proceed to the right, not because of the formation of an un-ionized acid or salt as in the case of calcite, but because of the much lesser solubility of  $\text{Ca}(\text{RCOO})_2$  as compared to the solubility of  $\text{CaF}_2$  (provided R is a hydrocarbon radical of sufficient size).

**Separation of Fluorspar from Quartz.**—No difficulty is experienced in separating fluorite from quartz. Sodium oleate, with or without pine oil and sodium silicate, gives satisfactory results.

Table 135 shows metallurgical results in one typical test run by members of the staff of the U. S. Bureau of Mines<sup>(4)</sup> on a relatively free-milling siliceous fluorspar ore. It is apparent

TABLE 135.—FLOTATION OF SILICEOUS FLUORSPAR ORE  
(After Coghill and Greeman.)

Product		Feed	Cleaner concentrate		Cleaner tailing	Tailing
Mineral content, per cent	$\text{CaF}_2$ . . . . .	67.9*	98.2		61.7	7.3
	$\text{SiO}_2$ . . . . .	27.9*	0.6		33.2	82.7
	$\text{CaCO}_3$ . . . . .	1.7	0.6		1.9	4.1
	$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ . .	2.4	0.6		3.1	5.9
Recovery, per cent	$\text{CaF}_2$ . . . . .		81.1		16.1	2.8
	$\text{SiO}_2$ . . . . .		1.2		21.2	77.6
	$\text{CaCO}_3$ . . . . .		18.5		19.8	61.7
	$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ . .		13.8		22.9	63.3
			Clean- ing	Rough- ing	Roughing and cleaning (cleaner tailing discarded)	
Selectivity indices	$\text{CaF}_2:\text{SiO}_2$ . . . . .		9.4	10.9	18.8	
	$\text{CaF}_2:\text{CaCO}_3$ . . . . .		2.3	7.5	4.4	
	$\text{CaF}_2:\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ . . . . .		2.9	7.7	5.2	

\* Calculated

that rejection of the silica is very good and that recovery of the fluorspar is satisfactory. Indeed, the selectivity index for the fluorspar-silica separation is better than the average selectivity indices obtained in flotation of most non-metallic minerals. The reagents used were as follows:

Reagent	Pound per Ton
Oleic acid . . . . .	1.0
Sodium oleate . . . . .	0.1
Sodium silicate . . . . .	0.2
Sodium carbonate . . . . .	0.2
Heavy crude pine oil . . . . .	0.2
Steam-distilled pine oil . . . . .	0.1

**Separation of Fluorspar from Calcite.**—Separation of fluorite from calcite has not been accomplished practically. This is to

be expected from the fact that both fluorite and calcite react very readily with fatty acids (Reactions [1] and [9]). Attempts to reduce the reactivity of the collector with the minerals in the hope of reaching a point where reaction proceeds with one mineral only have failed; these attempts have been made both with pH control and by using various fatty acids having relatively short hydrocarbon chains. However, separation of calcite from fluorite was obtained on a laboratory scale as follows: A mixture of free, deslimed calcite and fluorite was first conditioned in a hot solution of copper sulfate containing a generous amount of the copper salt, washed thoroughly, and floated with amyl xanthate. The calcite floated away from the fluorite with a characteristic yellow cast possibly due to the formation of a crust of copper xanthate at the surface. The consumption of reagents was large, but the tests are of interest as they indicate a possible means of effecting a calcite-fluorite separation.

A surprising feature of the data presented in Table 135 is that some selection between fluorite and calcite is shown. The partial rejection of lime is perhaps due to greater interlocking of the calcite and quartz than of these minerals with the fluorite, resulting in rejection of mixed quartz-calcite particles.

**Industrial Application.**—Calcite and quartz are the principal impurities in fluorspar ores. At present siliceous ores only can be treated by flotation for the production of acid-grade spar (that is fluorspar used in the manufacture of hydrofluoric acid). If the lime content of a calcareous fluorspar concentrate is not too high, leaching of the concentrate with dilute hydrochloric acid is not an economic impossibility, now that the price of hydrochloric acid has been much reduced.

It is said that a plant has operated intermittently on the flotation of fluorspar and that a recovery of 90 to 95 per cent of the fluorspar and rejection of 80 to 90 per cent of the silica has been obtained. These results are equivalent to a selectivity index of 8 or 10.

### PHOSPHATES

There are several varieties of calcium phosphate, some of which are crystalline (apatite) and others substantially amorphous. Crystalline phosphates contain certain negative ions, *e.g.*,  $\text{Cl}^-$ ,  $\text{F}^-$ , in partial replacement of the  $\text{PO}_4^{---}$  ion. The customary "bone phosphate" found in Florida and North

Africa is of the amorphous type; it contains substantial quantities of organic matter which cause it to assume a dark color. The western United States phosphate deposits which stretch from the Utah-Idaho line to British Columbia are finely oölitic in texture. Their fine texture requires a relatively large expenditure for liberation, but the Florida deposits are so loosely consolidated as to require little crushing and grinding for liberation to take place.

In unconsolidated organo-sedimentary deposits the principal impurity is silica. In the western oölitic deposits silicates, silica, and calcite are the principal impurities. In apatite deposits silicates, iron oxides, and calcite are commonly found.

If the gangue is siliceous, the phosphatic particles are readily floated, the reagents being essentially the same as for the flotation of fluorite or of calcite from silica: oleic acid, sodium silicate, and pine oil. Addition of sodium carbonate is sometimes desirable to adjust the pH to the optimum point. Generally a pH slightly under 8 seems to be most satisfactory.

**Organo-sedimentary Phosphates.**—Florida phosphates lend themselves particularly well to flotation even in a fairly coarse state. It is well known that, in Florida, phosphates occur as relatively coarse grains or pebbles loosely embedded in relatively fine sand. In dressing, the practice has been to wash the sand away from the coarse material, rejecting the sand. The latter, of course, contains a substantial amount of phosphate. It is for the treatment of these tailing sands that flotation appears to be best suited<sup>(16)</sup>.

In the treatment of Florida "rock," a relatively large amount of collector (2 to 4 lb. of oleic acid per ton of rock) is required. This is rather remarkable in view of the coarse state of subdivision of the feed; it may be traced to a resistance of calcium phosphate to react with collector anions. That is, reaction (10) may not proceed to the right as readily as reactions (9) or (1). Another cause whose importance is suggested by the greater floatability of apatite as compared with organic phosphates is the porosity of the organic phosphates.

Organic-phosphate froths present an unusual aspect caused perhaps by the coarseness of the particles in the froth: it is distinctly more oily or creamy than usual.

Table 136 presents some typical results obtained by U. S. Bureau of Mines investigators on Florida washery wastes. The

TABLE 136.—TYPICAL FLOTATION RESULTS ON PHOSPHATE WASHERY WASTES  
(After Lawrence and DeVaney.)  
Test A

Product	Weight, per cent	Assay, B.P.L.,* per cent	Insoluble, per cent	Phosphate recovered, per cent	Insoluble rejected, per cent
Feed . . . . .	100.0	48.5	37.4		
Concentrate . . . . .	54.6	75.1	4.3	84.6	
Tailing (including middling) . . . . .	45.4	16.4	77.1	....	93.7

Test B

Feed . . . . .	100.0	33.5	54.5		
Concentrate . . . . .	22.4	71.8	1.9	47.9	
Middling . . . . .	22.3	57.7	21.3	38.4	
Tailing . . . . .	55.3	8.3	89.2	....	90.5

\* B.P.L. is the customary abbreviation for "bone phosphate of lime" or tricalcium phosphate.

phosphate-insoluble selectivity index in test A was 9.1. The reagents used were approximately as follows (in pounds per ton): oleic acid, 1.6; crude pine oil, 0.8; steam-distilled pine oil, 0.6; sodium silicate, 0.25; sodium carbonate, 0.2.

Separation of organic phosphate from calcite has not been successful. Indications are that with ordinary reagents (soaps and pine oil) calcite is slightly more floatable than phosphate. It might be recalled that fluorite and calcite are almost equal in floatability (see above). The similarity in floatability in one case, and slight dissimilarity in the other, may be due to the difficulty in reaction (10) proceeding from left to right as compared to (9) and (1), because of relative insolubility of calcium phosphate as compared with calcium fluoride and calcium carbonate:



**Apatite Deposits.**—Although most phosphate deposits of commercial value are of organo-sedimentary origin, apatite, which is of igneous or metamorphic origin, may be abundant enough to justify exploitation. Also, apatite may occur as an impurity in magnetic iron ores. It has recently been found possible to concentrate magnetic iron ores by floating the apatite

from the magnetite, which is left in the tailing<sup>(18)</sup>. The reagent employed was sodium palmitate (about 10 lb. per ton).

Table 137 presents data obtained on a magnetite ore from the eastern United States containing apatite. The reagents used

TABLE 137.—FLOTATION OF A PHOSPHATIC MAGNETITE ORE

Product	Assays, per cent		Recoveries, per cent	
	PO <sub>4</sub>	Fe	PO <sub>4</sub>	Fe
Feed . . . . .	3.5	57.0		
Concentrate . . . . .	27.5	23.7	88.5	4.7
Tailing . . . . .	0.46	61.5	11.5	95.3

were sodium oleate (4 lb. per ton), pine-tar oil (0.2 lb. per ton), steam-distilled pine oil (0.2 lb. per ton), and sodium carbonate (1.0 lb. per ton). A satisfactory separation was obtained (selectivity index 12.5).

Separation of apatite from magnetite seems to result from the non-reaction of magnetite with fatty-acid anions at the pH at which flotation is conducted.

#### TUNGSTATES

The common tungsten minerals are scheelite, calcium tungstate, and wolframite, a ferrous tungstate in which manganese may replace iron. The strictly ferrous variety of wolframite is known as ferberite. Both scheelite and ferberite can be floated with soaps, the former somewhat more readily. Their flotation appears to depend on the formation of oriented coatings of calcium or iron soaps at the surface of the minerals. No difficulty is experienced in separating the minerals from siliceous material, but separation from calcite has, so far, been unsuccessful.

The high specific gravity of tungstates and the ease with which satisfactory separations are obtained on coarse sizes by gravity concentration indicate that, for some time to come, flotation will have to be an adjunct to gravity concentration unless the deposits involve the several minerals in an extreme complexity of association.

The frequent occurrence of calcium carbonate in tungsten deposits makes it impossible at present to secure universally high-grade concentrates. But a mixed calcite-tungsten concen-

trate lends itself to further concentration by leaching with a solvent for calcite, such as hydrochloric acid—leaving a substantially enriched concentrate as residue. Further flotation treatment of this residue, simply after pH adjustment, permits the rejection of the remainder of the siliceous material which is frequently contaminated by clayey and iron-bearing material formerly occluded in the calcite that has been dissolved by the acid leach. Following this procedure a concentrate containing about 70 per cent  $\text{WO}_3$  was obtained from a 1 per cent feed consisting exclusively of slime, with a recovery of about 70 per cent.

Table 138 presents some results obtained on a scheelite ore.

TABLE 138.—FLOTATION RESULTS ON A TUNGSTEN ORE CONTAINING 2.6 PER CENT TUNGSTEN AS SCHEELITE WITH QUARTZ AND CALCITE AS THE MAIN IMPURITIES

Product	Recovery, per cent				
	$\text{WO}_3$	Free CaO	Fe	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$
Recleaner concentrate. . . . .	78	78	20	3	1 5
Recleaner tailing . . . . .	13	11	18	6	6
Cleaner tailing . . . . .	5	7	23	15	12
Rougher tailing . . . . .	4	4	39	76	80.5

Selectivity indices after	$\text{WO}_3$ : free CaO	$\text{WO}_3$ : Fe	$\text{WO}_3$ : $\text{Al}_2\text{O}_3$	$\text{WO}_3$ : $\text{SiO}_2$
Roughing . . . . .	1.0	3.9	8 7	10 1
Roughing and cleaning . . . . .	1.1	4.1	10.1	11.6
Roughing, cleaning, and re- cleaning . . . . .	1.0	3.7	10.8	15 4

#### SULFATES

The only sulfates likely to be encountered in flotation problems are celestite ( $\text{SrSO}_4$ ) and barite ( $\text{BaSO}_4$ ), particularly the latter. Barite is fairly common as a gangue mineral in ores mined for some of the base metals. If sufficiently abundant in such ores, and if the ores are located reasonably near a barite-consuming center, the recovery of barite as a by-product may be of interest.

The problem may be economically attractive if the remainder of the gangue is siliceous, as barite commands a fair price particularly in the ground condition—and as the barite-recovering flotation operation is simple. On the other hand, if the remainder

of the gangue is partly or wholly a carbonate, the problem is unsolvable in the present state of knowledge.

Barite behaves toward soaps and fatty acids more like fluorite or apatite than like calcite, that is, reaction between mineral and reagent proceeds to form a superficial coating of soap at the mineral surface because of the relatively greater solubility of the mineral as compared to that of the soap rather than because of the formation of an undissociated acid. In view of the very small solubility of barite, a vivid picture of the great insolubility of the soaps that bring about collection is obtained.

Table 139 presents some results obtained in a typical instance

TABLE 139.—FLOTATION RESULTS ON A GALENA-BARITE ORE HAVING A SILICEOUS GANGUE\*

Product	Content, per cent			Recovery, per cent		
	Pb	Ba	SiO <sub>2</sub>	Pb	Ba	SiO <sub>2</sub>
Feed . . . . .	8 2†	27 4†	39 5†			
Lead concentrate . . . . .	62 2	4 7	4 1	97 3	2.2	1.3
Barite concentrate . . . . .	0 3	53 4	6 0	1.4	89 5	7.0
Tailing . . . . .	0.2	5.5	88.0	1.1	8.3	91.7

\* Reagents for lead flotation: pine oil, 0.1 lb. per ton; amyl xanthate, 0.12 lb. per ton; sodium carbonate, 2.0 lb. per ton; pH, 7.9.

Reagents for barite flotation: pine oil, 0.5 lb. per ton; sodium oleate, 2.0 lb. per ton; sodium silicate, 0.2 lb. per ton; hydrochloric acid, 0.25 lb. per ton; pH, 7.4.

† Calculated.

A barite flotation plant is in operation in the southwestern United States(24).

### OXIDES

Besides silica, the commonest and most important simple oxides encountered in nature are the oxides of iron, manganese, aluminum, titanium, and tin. Oxides of iron are magnetite (FeO.Fe<sub>2</sub>O<sub>3</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), and hydrated ferric oxides typified by limonite. The commonest oxides of manganese are psilomelane and pyrolusite (MnO<sub>2</sub>); aluminum occurs as the hydrated oxide, bauxite, and as the unhydrated crystalline oxide, corundum; titanium occurs as rutile (TiO<sub>2</sub>) and tin as cassiterite (SnO<sub>2</sub>).

**Iron Oxides.**—Substantial efforts to float the oxides of iron have not been made because of the present superabundance and low price of iron ores.



Magnetite and crystalline (specular) hematite may be expected to display fairly high floatability under proper conditions because of their relatively macrocrystalline condition, but hydrated oxides such as limonite may be refractory.

Specular hematite can be floated easily with various soaps<sup>(24)</sup>. It is activated by several metallic salts, but this effect may really correspond to improved pH rather than to genuine activation by the cation or anion of the added salt.

Mixtures of specular hematite and quartz cannot be separated by flotation except over narrow pH bands. Best selection is

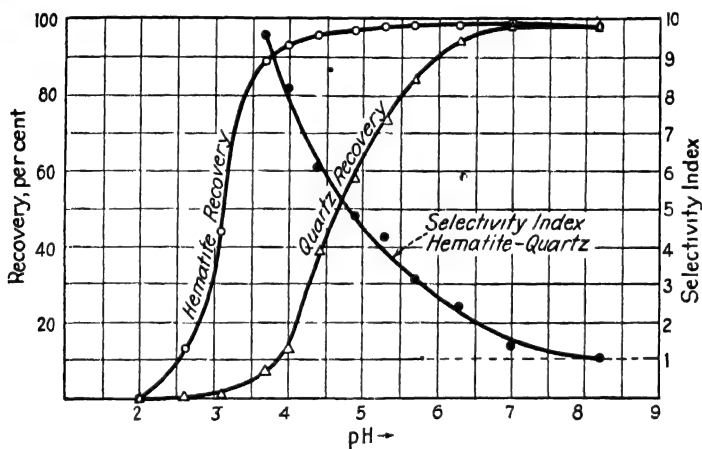


FIG. 98.—Separation of specular hematite from quartz.

Effect of pH on 1:4 mixtures of 100/600-mesh particles. Reagents: Pine oil, 0.2 lb. per ton; sodium oleate, 1.0 lb. per ton; HCl to suit.

obtained in the vicinity of pH 3.5 to 4.0 (also of pH 7.5 to 9.0 in a soda-ash circuit). Figure 98 shows the recovery of hematite and quartz from synthetic mixtures over the pH range 2 to 8, and the selectivity index over the pH range 3.7 to 8.2.

Magnetite is more refractory to flotation than hematite, perhaps because of the much lesser solubility of  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  than of  $\text{Fe}_2\text{O}_3$  in aqueous solutions. If calcite or apatite is the gangue, the phosphatic or carbonate material can be floated, leaving the iron in the tailing<sup>(18)</sup>.

**Manganese Oxides.**—It has recently been reported that manganese dioxide ores have been concentrated by flotation<sup>(30)</sup>. If the mineral is macrocrystalline it is not surprising that concentration is possible, particularly if the gangue is siliceous; but,

if the gangue is calcareous, flotation of the calcareous material precedes that of the manganese dioxide or occurs simultaneously.

The reagents used by the U. S. Bureau of Mines' investigators were substantially the same as are required for the flotation of other non-metallic minerals, namely soap or oleic acid for collection, pine oil for frothing, waterglass for silica inhibition, and alkaline salts for pH regulation. Earlier experiments performed in the writer's laboratory indicated no separation of manganese dioxide from associated minerals. These experiments were made using the same reagents in substantially the same proportions as the Bureau of Mines' experiments, failure being caused by the slimyness of the ores tested and by the unsatisfactory liberation of the minerals that resulted in spite of the fineness of grinding.

Table 140 shows the type of results that may be obtained in the flotation of manganese ores under favorable conditions of texture and structure.

TABLE 140.—FLOTATION OF A PYROLUSITE MANGANESE ORE  
(After DeVaney and Clemm.)

Product	Content, per cent		Recoveries, per cent	
	Manganese	Insoluble	Manganese	Insoluble
Feed . . . . .	25 3	54		
Concentrate . . . . .	56 0	4	91	3
Middling . . . . .	16.7	67*	5	9*
Tailing . . . . .	2.0		4	88*

\* Estimated (A M G)

Approximate manganese—insoluble selectivity indices: roughing, 13 3; cleaning, 7 4; roughing and cleaning, discarding cleaner tailing, 18 1

**Aluminum Oxides.**—Bauxite can be floated<sup>(7)</sup> to some extent from siliceous gangue, but the separation is not good. This is perhaps caused, in part, by the unsatisfactory liberation of the minerals. Typical results are presented in Table 141. The necessary reagents include, as usual, fatty acids and pH-controlling alkaline salts, such as sodium sulfide.

No data are reported concerning corundum ( $\text{Al}_2\text{O}_3$ ) and spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ). In view of their being composed of oxides capable of forming insoluble soaps, it is likely that these minerals can be concentrated by flotation, if the gangue is siliceous and if the concentrates are acceptable in finely ground condition.

TABLE 141.—TYPICAL FLOTATION RESULTS OBTAINABLE ON LOW-GRADE SILICEOUS BAUXITE  
(After Gandrud and DeVaney.)

Product	Weight, per cent	Content, per cent		Recoveries, per cent	
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Concentrate. . . . .	64.8	58.5	4.4	72.4	19.2
Middling . . . . .	5.0	48.3	21.5	4.6	7.3
Tailing. . . . .	30.2	39.7	36.0	23.0	73.5
Feed (composite). . . . .	100.0	52.3	14.8		

Alumina-silica selectivity indices: After roughing, 3.1; after cleaning, 2.4; after roughing and cleaning, discarding cleaner tailing, 3.3

**Tin Ores.**—Flotation has been applied in two ways to the concentration of tin ores. One application has consisted in a removal of pyrite from gravity concentrates by floating the pyrite from the ground pulp. This can be done very satisfactorily, but if any tin occurs as sulfide (as in some Bolivian ores), the sulfide tin may be floated with the pyrite and lost. Table 142 shows that excellent results can be obtained on ores in which no sulfide tin occurs.

TABLE 142.—FLOTATION OF PYRITE FROM CASSITERITE CONCENTRATE

Product	Metal content, per cent		Recovery, per cent <sup>1</sup>	
	Fe	Sn	Fe	Sn
Feed (composite) . . . . .	9.4	59.2		
Concentrate . . . . .	41.4	3.1	91	1.1
Tailing. . . . .	1.1	75.5	9	98.9

<sup>1</sup>Selectivity index, pyrite, cassiterite, approximately 30.

The other application of flotation to the concentration of oxide tin ores has aimed at floating the cassiterite from the associated silicate gangue with which cassiterite frequently occurs. Efforts in this direction have been stimulated by the relatively high value of tin and by the suitable physical condition (for flotation operation) of the fine tailings of gravity concentrating plants.

Several kinds of reagents have been proposed among which are cupferron (ammonium salt of nitrosophenyl hydroxylamine) and certain complex fatty substances (*e.g.*, salts of taurocholic acids), occurring in substantial proportion in slaughter-house wastes<sup>(31)</sup>. In spite of attempts made in the author's laboratory to float cassiterite from silica and silicates by means of cupferron, no particular success was obtained.

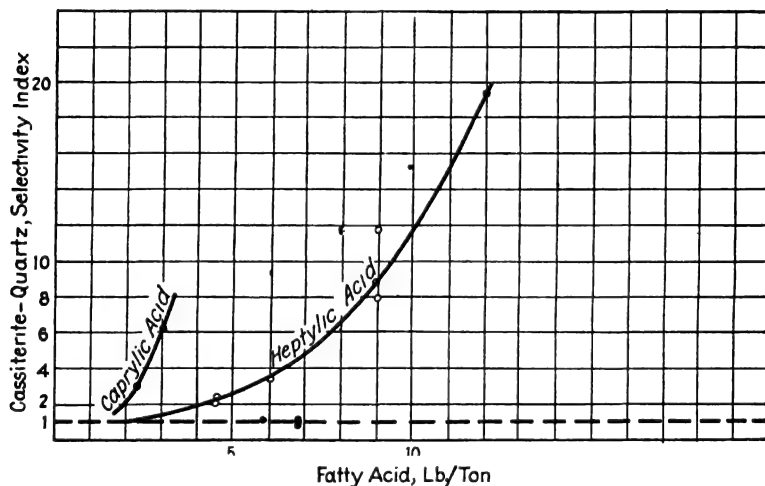


FIG. 99. Separation of cassiterite from quartz.  
Effect of increasing amounts of heptylic and caprylic acid on 1:4 mixtures of 100/600-mesh particles.

On the other hand, very good results have been obtained by the use of fatty acids or soaps and sodium silicate with close pH control in the treatment of clean siliceous ores<sup>(5)</sup>.

Figure 99 shows the effect of increasing amounts of heptylic and caprylic acids in the flotation of quartz-cassiterite mixtures (pH unrecorded; probably below 6.5)<sup>(8)</sup>. Increase in selection results from increase in collector concentration. Although no pH data are available, flotation was probably conducted at a lower pH in the tests involving a large amount of collector.

Tests were conducted on an ore consisting essentially of cassiterite, quartz, feldspar, white mica (sericite), and tourmaline, the bulk of the ore being quartz and feldspar. The tin content of the feed was about 0.8 per cent. Roughing flotation, using soap and sodium silicate with close pH control, led to the production of a rougher concentrate containing 6 to 10 per cent tin

and a tailing containing 0.06 to 0.10 per cent tin. This corresponds to a selectivity index of about 10 and a tin recovery of the order of 90 per cent. Cleaning of the concentrate could easily be carried to yield a product containing 25 to 35 per cent tin, but further cleaning was found difficult because the mica and tourmaline had become concentrated in the rougher concentrate and were much more difficult to reject than feldspar and quartz. In spite of the difficulties, repeated cleaning and care in avoiding overuse of any reagents permitted the production of a final concentrate assaying about 50 per cent tin and containing about 70 per cent of the total tin, the remainder of the metal being distributed among the rougher tailing and the several cleaner tailings.

Handy and Beard<sup>(9)</sup> find that copper sulfate favors the flotation of cassiterite over associated gangue minerals. They also claim that desliming the ore pulp previous to flotation is helpful. Although comparison between tests involving copper sulfate and tests in which copper sulfate was absent, and between slimy and deslimed pulps are not available, good concentration was obtained by the patentees (Table 143).

TABLE 143.—FLOTATION TESTS\* ON DESLIMED CASSITERITE ORE FROM BOLIVIA  
(After R. S. Handy.)

Product	Weight, per cent	Tin assay, per cent	Tin re- covery, per cent
Flotation tailing . . . . .	67.4	0.07	0.6
Flotation middling . . . . .	7.2	2.38	2.3
Flotation concentrate . . . . .	25.4	30.7	97.1
Table concentrate from flotation concentrate	14.7	50.4	96.6
Table tailing from flotation concentrate	10.7	0.36	0.5
Magnetic residue from table concentrate	9.6	76.0	95.6
Magnetic product from table concentrate	5.1	1.47	1.0

\* Using 2.0 lb. of a jelly-like mixture of oleic acid, cresol, sodium carbonate, and sodium silicate per ton of ore.

### SILICATES

Silicates may be considered as compound oxides of silica and of the metals.<sup>1</sup> For instance, potash feldspar may be considered as

<sup>1</sup> Although in accord with older concepts, this is not strictly true according to x-ray studies (<sup>1a</sup>), but it provides a simple approach for preliminary study of the floatability of silicates.

$K_2O \cdot Al_2O_3 \cdot 6SiO_2$ , olivine as  $(R''O)_2 \cdot SiO_2$ , beryl as  $(BeO)_3 \cdot Al_2O_3 \cdot 6SiO_2$ , etc. The surface of the silicates may therefore be regarded as composed partly of non-floatable silica, partly of soluble unfloatable alkali oxides or water, and partly of insoluble oxides of metals capable of becoming floatable if allowed to react with alkali soaps to form exceedingly insoluble soaps. Although different metals probably have different tendencies to form insoluble soaps they may be considered, as a first approximation, as capable of forming these soaps equally well. Since each divalent metal should be capable of appropriating two fatty-acid radicals, and each trivalent metal, three, an estimate of the relative floatability of silicates deducible from the above reasoning has to take this into consideration. If, then, each particle of pure (unactivated) silicate mineral is really a microtextured middling particle consisting of juxtaposed patches of unfloatable  $SiO_2$  and  $R_2O$ , and of floatable  $RO$  and  $R_2O_3$ , (counting each  $SiO_2$ , each  $R_2O$ ,  $RO$  and  $\frac{1}{3} R_2O_3$  as unity), the ratio of floatable to non-floatable surface for different silicates is as shown in Table 144. This tabulation has no experimental foundation. However, its plausibility is substantiated by the observed facts that silica in the inactivated state is not collected by soaps and fatty

TABLE 144.—HYPOTHETICAL RELATIVE FLOATABILITY (IF SOAPS OR FATTY ACIDS ARE USED) OF VARIOUS SILICATES

Mineral	Formula	Units of unfloatable surface	Units of floatable surface	Ratio of floatable to unfloatable surface
Quartz	$SiO_2$	1	0	0
Feldspars	$\begin{cases} (KNa)_2O \cdot Al_2O_3 \cdot 6SiO_2 \\ CaO \cdot Al_2O_3 \cdot 6SiO_2 \end{cases}$	 7 6	 3 4	 0.43 0.67
Feldspathoids (leucite) . . . .	$(KH)_2O \cdot Al_2O_3 \cdot 4SiO_2$	5	3	0.60
Talc . . . . .	$H_2O \cdot 3MgO \cdot 4SiO_2$	5	3	0.60
Spodumene . . . . .	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	5	3	0.60
Kaolin . . . . .	$2H_2O \cdot Al_2O_3 \cdot 2SiO_2$	4	3	0.75
Serpentine . . . . .	$2H_2O \cdot 3MgO \cdot 2SiO_2$	4	3	0.75
Muscovite . . . . .	$4(HK)_2O \cdot 3Al_2O_3 \cdot 6SiO_2$	10	9	0.90
Beryl . . . . .	$(BeO)_3 \cdot Al_2O_3 \cdot 6SiO_2$	6	6	1.00
Pyroxene . . . . .	$R''O \cdot SiO_2$	1	1	1.00
Amphibole . . . . .	$R''O \cdot SiO_2$	1	1	1.00
Chlorite . . . . .	$4H_2O \cdot 5(MgFe)O \cdot Al_2O_3 \cdot 3SiO_2$	7	8	1.15
Biotite . . . . .	$(HK)_2O \cdot 2(MgFe)O \cdot Al_2O_3 \cdot 3SiO_2$	4	5	1.25
Epidote . . . . .	$(CaO)_4 \cdot (Al_2O_3)_3 \cdot H_2O \cdot 6SiO_2$	7	13	1.85
Olivine . . . . .	$(R''O)_2 \cdot SiO_2$	1	2	2.00
Garnet . . . . .	$(R''O)_3 \cdot (R_2'''O)_2 \cdot (SiO_2)_3$	3	9	3.00
Andalusite . . . . .	$Al_2O_3 \cdot SiO_2$	1	3	3.00

acids, but that slaked lime, hematite, and alumina (the principal metal oxides involved) are collected by soaps without activation. From Table 144 it might be inferred that the silicates can be arranged approximately as follows in order of increasing floatability:

1. Silica.
2. Feldspars, feldspathoids, talc, kaolin, spodumene, serpentine.
3. Micas, chlorite, beryl, pyroxene, amphibole.
4. Epidote, olivine.
5. Garnet, andalusite.

It is interesting to note the broad agreement between this theoretical sequence and an incomplete sequence obtained experimentally.

**Feldspars.**—Feldspars are poorly floated by soaps if all activation by metallic cations is avoided. However, they are somewhat

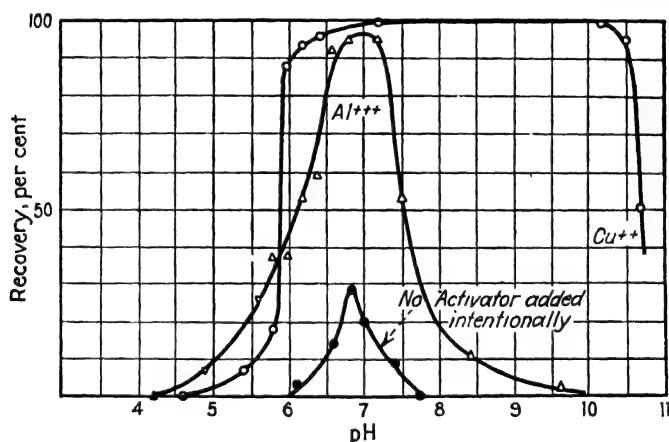


FIG. 100.—Activated feldspar.

Effect of pH on the recovery of 100/600-mesh particles, activated by copper or aluminum nitrate, 1.0 lb. per ton, using sodium oleate, 0.20 lb. per ton, terpeneol, 0.20 lb. per ton, and NaOH or HCl to suit.

more floatable than quartz (*e.g.*, albite shows a 30 per cent recovery at optimum pH against 10 per cent for quartz at its optimum pH, using 1.0 lb. sodium oleate per ton).

Variations in the floatability of the various feldspars have been noted, lime feldspars appearing to be the most floatable.

Like quartz, feldspars are readily activated by salts of cations capable of forming insoluble soaps (Fig. 100). Activation takes place at a lower metal-salt concentration than activation of

quartz, but this activation is difficultly made complete (Fig. 101). The less complete activation of feldspar than of quartz is perhaps to be correlated with a porosity of surface in the feldspar resulting from solution of  $K_2O$ ,  $Na_2O$  or  $CaO$  during desliming of the feldspar used in the tests presented in Fig. 101. That feldspars dissolve selectively in water, leaving behind a silica skeleton, is suggested by the fact that they yield a distinctly alkaline reaction in water (pH *ca.* 8.0) instead of a slightly acid or neutral reaction such as is obtained with quartz (pH 6.0 to 7.0). If feldspars are indeed

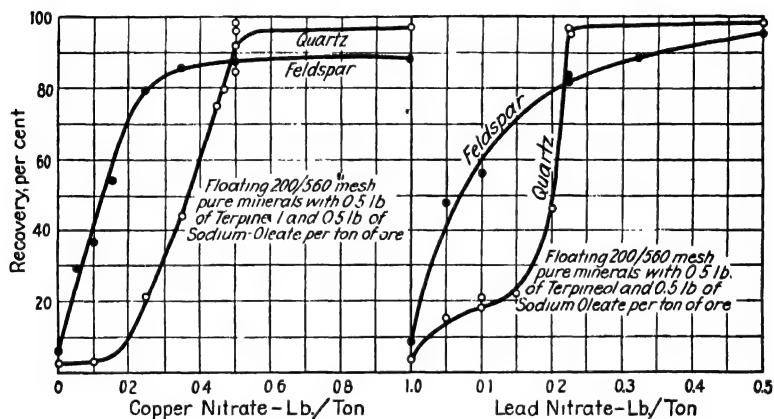


FIG. 101.—Separate flotation of quartz and feldspar. The same reagents were used in testing each mineral.

selectively dissolved by water, their surface must be a sponge-like silica skeleton suggestive (except for the presence of atomic orientation) of the sponge-like skeletons remaining at the surface of glass after contact with acids<sup>(6)</sup>. Such a sponge-like surface would probably present an enhanced adsorptive capacity, just as platinum black presents an enhanced adsorptive capacity over that of sheet platinum. Also, a sponge-like feldspar surface could accommodate more adsorbed ions than a relatively smooth quartz area of same apparent surface. Thus, if feldspar does have a selectively leached surface it should be, both, more readily activated than quartz and require more activator per unit of apparent surface to be fully activated. The leached-surface hypothesis concerning feldspar accounts for the observed behavior of that mineral in comparison with quartz (Fig. 101).

**Separation of Feldspar from Quartz.**—Some separation of feldspar from quartz can be made by careful pH control or by



careful limitation of the amount of activator and of collector, or better still, by a combination of these factors. At best the separation is poor, as may be seen from Fig. 102.

**Experiments with a Feldspathic Sericite.**—A finely foliated mica-schist consisting of fine-grained sericite and relatively coarse, granular feldspar was concentrated by flotation for the production of wall-paper mica. Excellent separations were obtained after grinding to 100 mesh through the use of about 1.5 to 2.0 lb. of sodium oleate per ton at a pH of about 8.0.

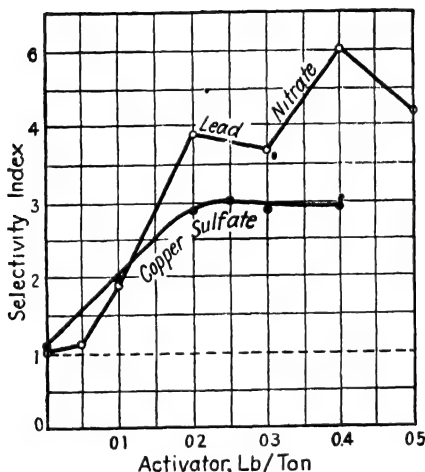


FIG. 102.—Separation of quartz from feldspar.

Reagents: terpeneol, 0.5 lb. per ton, sodium oleate, 0.5 lb. per ton, and activator as shown. (1:1 mixture of 100/600-mesh particles).

Approximately 90 per cent of the mica was recovered and 90 per cent of the feldspar was rejected. In this instance the structural condition of the ore, that is the flakiness of the mica combined with the granular character of the feldspar, was no doubt a factor in promoting the separation.

**Experiments with a Garnetiferous, Feldspathic Sericite Schist.**—A finely foliated mica-schist similar to the above, with the exception of the added complexity provided by the garnet, was concentrated for the production of tire-casing mica filler. The garnet was of the iron-bearing variety known as almandite and occurred to the extent of a few per cent as fine grains peppered through the schist. Its removal was essential to the production of a usable casing filler. The garnet floated with the sericite

if enough soap was added to float the latter, but ahead of it under starvation conditions. Table 145 presents typical results.

TABLE 145.—FLOTATION OF A GARNET-MICA-FELDSPAR SCHIST

Product	Mineral content, per cent*			Approximate recovery, per cent		
	Garnet	Mica	Feldspar	Garnet	Mica	Feldspar
Feed.....	8	80	12			
Garnet concentrate ..	45	53	2	88	11	2.5
Mica concentrate. . .	1	98	1	8	73	4.5
Tailing.....	1	52	48	4	16	93

\* Estimated microscopically.

The data presented in Table 145 indicate selectivity indices of 7.7 between garnet and mica and of 16.9 between garnet and feldspar in the garnet-floating cycle, and of 9.7 between mica and feldspar in the mica-floating cycle.

**Experiments with a Pyroxene and Feldspar-bearing Garnet Middling.**—The feed used in the experiments was a middling resulting from gravity concentrating operations; it contained about 65 per cent garnet. Particularly good flotation results were obtained in separating the garnet from the other silicates in this relatively coarse middling (35 to 150 mesh) if the pulp were first treated in dilute acid and washed. The improvements in results should perhaps be ascribed to a cleansing action on the part of the acid on certain mineral particles, or to the fact that after a certain number of washings the pulp was at the proper pH

TABLE 146.—TYPICAL RESULTS IN FLOTATION OF A GARNETIFEROUS MIDDLING

Product	Mineral content, per cent*			Approximate recovery, per cent		
	Garnet	Pyroxene	Feldspar and quartz	Garnet	Pyroxene	Feldspar and quartz
Feed .....	54	25	10			
Concentrate	95	4.5	0.5	92	11	3
Tailing .....	14	60	26			

Garnet-pyroxene selectivity index, 9.7; garnet-quartz-feldspar selectivity index, 19.2.

\* Estimated microscopically.

for selection. (This work was done before the importance of pH control in flotation was fully realized.) Typical results obtained after treatment with a 10 per cent  $\text{H}_2\text{SO}_4$  solution, washing and flotation with oleic acid (0.3 lb. per ton) and terpeneol (0.2 lb. per ton) are presented in Table 146.



## CHAPTER XIV

### MACHINERY

A detailed study of the machinery used in flotation plants is beyond the scope of this book. But a full understanding of the practical and economic features of the process requires a general acquaintance with mill machinery, and more particularly with that machinery pertaining to the flotation division and to related mill divisions, namely the concentrate and tailing disposal divisions.

A knowledge of the machinery required for crushing, grinding, screening, classifying, sampling, storing, and conveying the ore ahead of the flotation division is, of course, necessary; but as the subject is fully treated in several standard works<sup>(13)(12)(14)(9)</sup>, it is not necessary to cover it anew.

Besides flotation cells, the machinery of particular interest to flotation involves a number of auxiliary units whose object is to carry on complementary operations. Auxiliary machinery includes pulp distributors, conditioning tanks, reagent feeders, air compressors, thickeners, filters, pulp samplers, pulp-conveying devices, to which may be added grinding mills and classifiers if regrinding is used.

### FLOTATION MACHINES

**Requirements.**—To be successful a flotation machine must fulfill certain conditions, some of which aim at the production of good metallurgy, and others at simplicity and low cost of operation.

From a technical standpoint a flotation machine is subject to the following requirements: it must (1) be continuous in operation, (2) generate fine air bubbles, (3) disperse these bubbles in the pulp as thoroughly as possible, (4) separate the mineralized bubbles, as a froth, from the pulp, (5) discharge the froth in a suitable container.

Condition 1 is as obvious as general to all industrial operations; 2 connotes the use of reagents whose molecules adsorb at gas-liquid boundaries and a certain amount of agitation; 3 indicates

that circulation of the pulp is desirable; 4 signifies that a relatively quiescent zone in which creaming proceeds is necessary; and 5 signifies that froth removal by mechanical scraping, or natural overflow following creaming is desirable.

From an operating standpoint a flotation cell must be simple, accessible, easily adjusted, have infrequent shut-downs of short duration, low power cost, and require the minimum of attention with fluctuations in ore character.

Simplicity implies low cost; accessibility favors quick repairs; easy adjustment minimizes operating difficulties. The definite value to the operator of the other qualifications is so obvious as to necessitate no comment.

**Principles.**—Flotation machines are often composed of several identical *cells* arranged in series, that is in such a way that one cell receives as feed the defrothed pulp from the preceding cell. Some flotation machines are composed of single cells having great length in comparison with their width.

Flotation cells are of four principal types in accordance with the mode of introduction of the gas:

1. *Agitation cells* in which air is drawn by a vortex caused by a rotating impeller.

2. *Sub-aeration cells* in which air is introduced by suction or by blowing through or to the base of a rotating impeller.

3. *Cascade cells* in which air is introduced by tumbling of the pulp.

4. *Pneumatic cells* in which air is introduced directly by blowing.

Combination machines have been designed, featuring more than one mode of gas introduction.

A great number of flotation machines have been patented, but the number that have been used at all extensively is small. A substantially complete list with descriptions being available elsewhere<sup>(13)</sup>, only the most widely used or typical machines are described here.

**Minerals Separation Agitation Machine.**—The best known agitation machine is the Minerals Separation "Standard" machine.<sup>1</sup> It consists essentially of a number of cells (8 to 16) arranged in series. Each cell consists of an agitating compartment and a froth-separating compartment or spitzkasten. Agitation is produced by a cross-bladed, vertical impeller rotating

<sup>1</sup>A development from, and improvement over, the Hoover machine (Fig. 1, p. 4).

at high speed and drawing air into the pulp by the vortex which it forms. The spitzkasten derives the name from its pointed shape.

The feed enters the first agitating compartment, is thrown out through a slot entering the spitzkasten where it separates into a froth which is raked into an overflow launder, and a defrothed pulp which passes to the bottom of the agitating compartment in the next cell. Flow from a spitzkasten to the following agitating compartment is regulated by means of a valve actuated by a hand wheel. A power-driven scraper pushes the froth into a concentrate launder. The cells are generally gear driven from a horizontal lineshaft.

M.S. Standard agitation machines are being replaced by sub-aeration machines but a large number are still in operation.

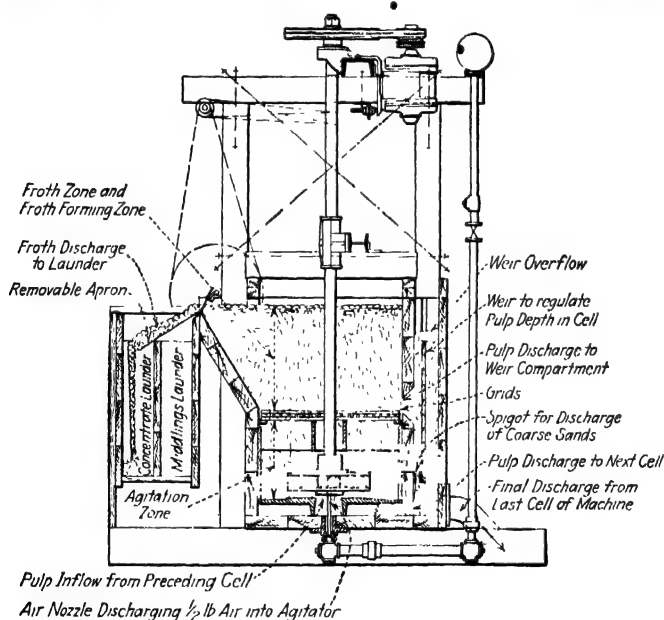


FIG. 103.—Diagrammatic sketch of Tex-rope driven sub-aeration M. S. machine. (Minerals Separation North American Corp.)

**Other Agitation Machines.**—Many agitation machines have been built. Essentially they are variants of the M.S. machine, that is, they involve an agitating compartment and a froth-separating compartment, a vertical impeller with cross-blades, and series flow from cell to cell.

Some agitation machines have departed from the M.S. design by the use of a horizontal-spindle agitator (Eberenz and Brown, U. S. Patent 1,187,822/1916; Mishler, U. S. Patent 1,197,843/1916), or by the use of a centrifugal pump as agitating compartment (Colburn and Colburn, 1,226,062; 1,226,063/1917; Hydrotator flotation machine).

**M.S. Sub-aeration Machine.**—Figure 103 shows the M.S. sub-aeration machine. This machine differs from the Standard

TABLE 147.—NORMAL CAPACITIES, M.S. SUB-AERATION MACHINES;  
TONS OF ORE PER 24 HR.

Based on 1 min. treatment per cell, and ore in place at 11 cu. ft. per ton (*Manufacturers' Data.*)

Ratio of water to ore	Diameter of agitator, inches					
	10	12	15	18	21	24
	Size of cell, inches					
	18½	23¼	27¼	31¼	37¼	42
2:1	48	120	210	340	560	800
2½:1	40	100	175	280	470	650
3:1	34	85	150	240	400	550
3½:1	29	75	130	210	350	480
4:1	26	65	115	180	300	425
4½:1	23	60	105	160	270	380
5:1	21	55	95	150	250	350
5½:1	19	50	85	135	230	320
6:1	18	45	80	125	210	290

No increase in the treatment time due to the removal of concentrate or deduction for the middling return is made in the above table. Unless the middling return is greatly in excess of the amount of concentrate removed, no allowance need be made in using the table.

The number of cells required to treat a given tonnage is proportional to the tabulated tonnage, the time of treatment remaining 1 min. per cell.

To determine the number of M.S. sub-aeration cells of a given size, multiply treatment time in minutes by proposed tonnage per 24 hr. and divide by tabular value corresponding to size of machine and given pulp density.

*Example.*—Number of 42-in. cells with 24-in. agitators to give 20 min. treatment to 240 tons per 24 hr. at 3 to 1 pulp =  $\frac{20 \times 240}{550} = 8.8$ . Next higher even number of cells = 10.



machine in many respects besides the mode of air introduction. Among these differences, the abolition of the division between agitation and froth-separating compartments is the most obvious. This permits the top of what was formerly an agitation compartment to act as froth-separating zone, so that, as far as froth separation is concerned, a cell of smaller volume does the work of a larger cell. The introduction of a grid half way up the cell prevents turbulence in the froth-separating zone; that of a removable apron permits a skimmer to direct the froth into either the concentrate or middling launder. Tex-rope drive is generally used.

Capacity of the cells, as given by the makers, is presented in Table 147.

The following advantages are claimed for M.S. sub-aeration machines:

1. All the pulp must pass through each agitator as it flows through the machine.

2. Any desired depth of pulp in each cell can be maintained, irrespective of the other cells. This feature is obtained by means of the overflow weirs placed at the back of the cells.

3. Any cell or cells can be used for conditioning purposes without disturbing the other cells. This is accomplished by removing the slats from the overflow weir, thus lowering the pulp level below the point where the froth will overflow the froth lip.

4. Reagents can be added at any point in the flow. This makes possible step reagent addition or conditioning, which is often desirable.

5. One or more middling products can be returned to the same machine.

6. The first cell or cells can be used as cleaner by introducing the flotation feed into the next following cell. The tailing from the cleaner cells automatically enters the same cell as the flotation feed.

**Denver "Sub-A" Machine.**—The Fahrenwald or Denver "Sub-A" machine is similar to the M.S. sub-aeration machine from which it differs in some details of air inflow, pulp transfer from one cell to another and impeller construction<sup>(3)</sup>.

Figure 104 shows diagrammatically a double-overflow cell (with air bubbles much magnified). This machine features lessened floor-space requirements per ton of daily plant capacity.

Figure 105 shows V-rope drive (similar to Tex-rope drive) for an eight-cell machine.

The makers claim that compressed air is generally unnecessary since the suction about the impeller draws enough air for practical

purposes. By comparison it might be noted that  $\frac{1}{2}$  lb. air is recommended for the M.S. sub-aeration machine.

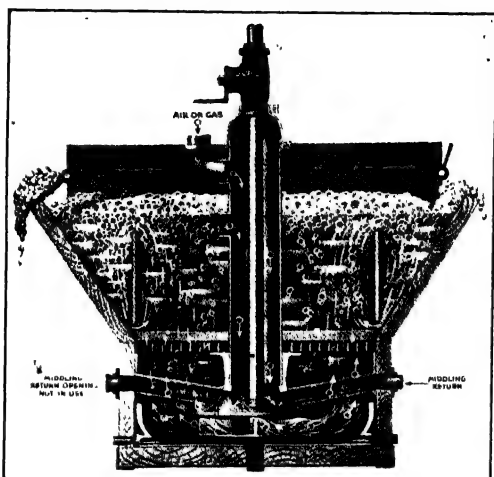


FIG. 104.—Denver sub-aeration-cell. (*Denver Equipment Co.*)  
Double overflow machine showing aeration and circulation.

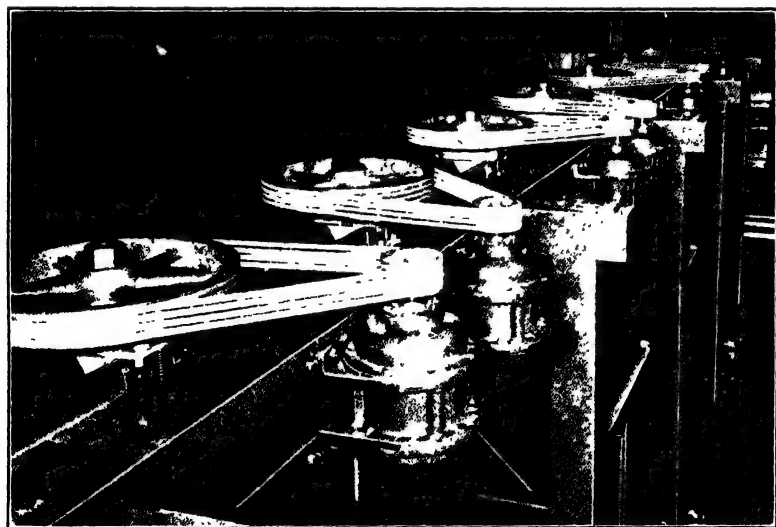


FIG. 105.—Denver sub-aeration machine showing motors and "V-rope" drive.  
(*Denver Equipment Co.*)

**Kraut Machine.**—Figure 106 shows, in section, the new Kraut machine. The machine consists of a number of cells. In each

cell is suspended a stationary conical vessel *a*. Within this vessel is made to rotate a similarly-shaped hollow truncated-conical rotor *b*, the outer surface of which is provided with a series of projecting helical riffles. The walls of the rotor have apertures

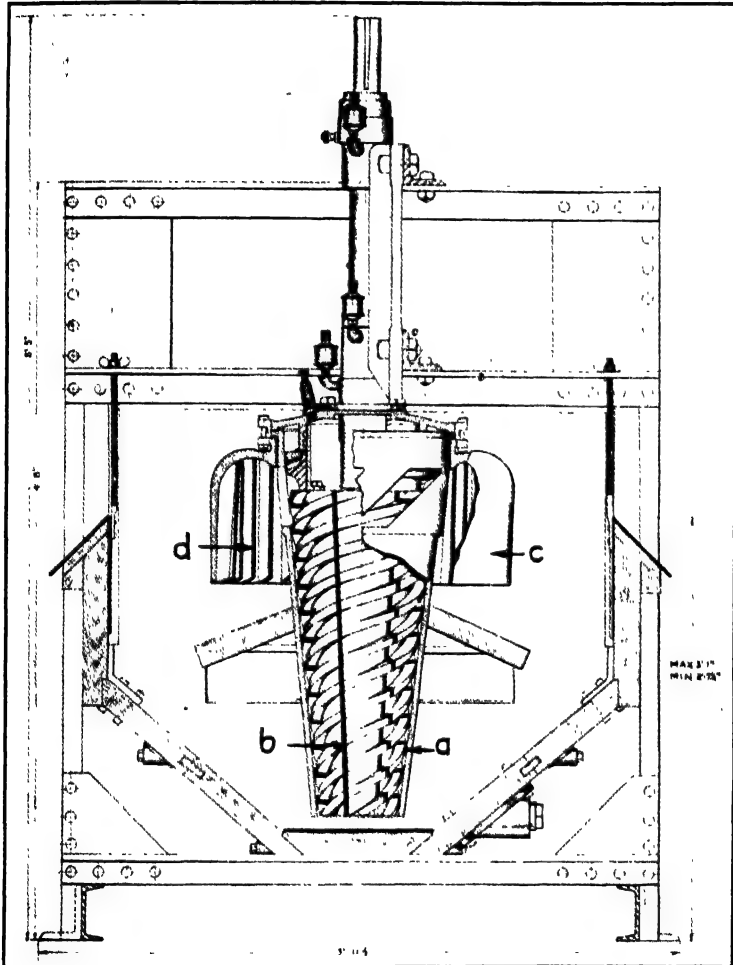


FIG. 106.—Kraut machine. (*Pan-American Engineering Corp.*)  
Sectional view.

for the passage of air, and the interior of the rotor communicates with the atmosphere through a valve-controlled air passage. The upper parts of the stationary conical vessel and the revolving

rotor are overhung by a bell-shaped vessel *c*, open at the bottom, and on its inside wall provided with a series of baffles.

The pulp passes at the bottom into the interspace between the stationary cone and the revolving rotor and is elevated to the top and discharged into the space below the bell. The air admitted through the control valve to the interior of the rotor is drawn into the rising pulp through the openings provided in the wall of the rotor, the amount of air admitted determining the degree of vacuum maintained under *c*. The aerated pulp underneath the bell is brought to rest by means of the baffles *d* on the inside of *c*. On discharge from under *c*, the pulp comes to rest gradually as it moves downward, part of the pulp circulating back to the bottom intake, part passing on to the next cell for retreatment. The froth rises to the surface on top of the pulp level in the tank and builds up until it overflows the edges of the tank into the concentrate discharge lips on both sides of the machine.

Adjustable gates on the sides of the tank provide a means to raise the height of the concentrate column as may be desired, and also permit taking care of the hydraulic gradient required to pass the pulp through the machine from the feed to the tailing end. The pulp level is adjusted by means of a weir overflow at the discharge end of the machine. An auxiliary sand discharge is provided to clean the machine in case of sand accumulations.

The Kraut machine is a recent introduction and it is not known how well it will stand the rough test of practice. Preliminary reports indicate metallurgical results on a par with those of the best competing machines. However, the small clearances and high impeller speed suggest higher-than-average wear.

**Other Sub-aeration Machines**<sup>(13)(7)</sup>.—Some of the better known sub-aeration machines are the Fagergren and Green (U. S. Patent 1,195,453/1916), Groch (U. S. Patent 1,276,753/1918; 1,413,723/1922), Ruth (U. S. Patent 1,445,042; 1,463,405/1923), and Hebbard machines.

**The K. and K. Sub-aeration-cascade Machine.**—This (Fig. 107) is one of the few machines using cascade action that has been used industrially. The essential parts are an aerating and a froth-separating compartment. Aeration is produced by a horizontal hollow cylinder about 9 ft. long and 30 in. in diameter, revolving at 160 to 200 r.p.m. The air flows out through holes in the aerating cylinder and is also sucked through a special

pipe into the agitating compartment. Suitable baffles and ports assure pulp circulation.

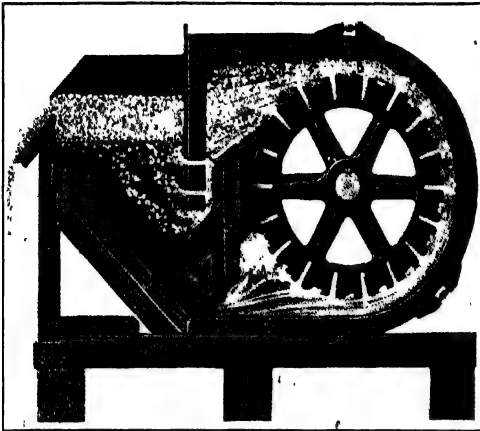


FIG. 107.—Standard single-spitz K. & K. machine. (*Southwestern Engineering Corp.*)

**Janney Mechanical-air Machine.**—The Janney machine utilizes mechanical agitation and pneumatic gas introduction. It is in

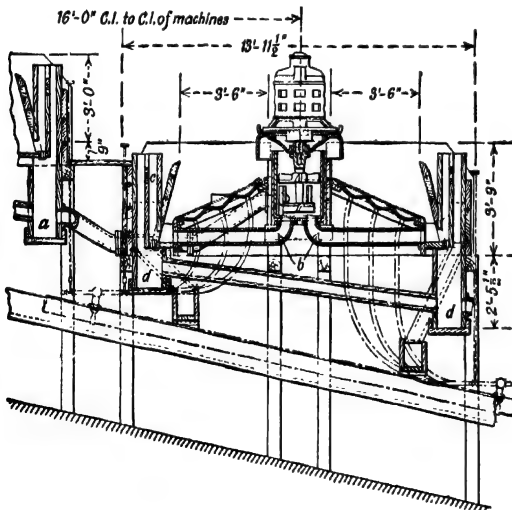


FIG. 108.—Janney mechanical-air machine. (*After Taggart.*)

substance a double-overflow agitation machine fitted with air baskets in the froth-separating compartments (Fig. 108) The

agitator consists of two sets of blades mounted on a vertical spindle connected directly to a vertical-spindle motor. The air baskets are supplied with air at 4- to 5-lb. pressure.

The Janney machine has been installed at the Utah Copper Company's plants where some 1400 units are in use. Its success on Utah Copper Company's ores has been striking.

**Callow Machine.**—Callow cells (Fig. 109) consist of rectangular sloping-bottom troughs with vertical sides and ends fitted with a canvas bottom through which air is blown by a blower or compressor. Usual dimensions are about 9 ft. in length, 30 in. in width, 4 ft. in depth at the discharge end, and 18 in. at the feed end. The blankets consist of three or four layers of canvas or palma twill of medium weight. They are supported on a screen fastened to the top of a basal air box. The air box is divided into compartments; this permits regulation of the air pressure and balancing for differences in hydrostatic head.

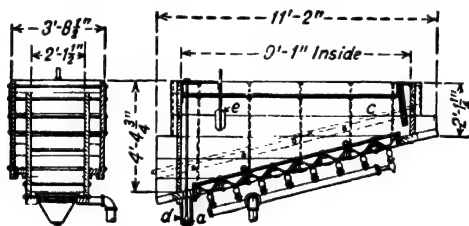


FIG. 109.—Callow-pneumatic machine. (*The General Engineering Co.*)

The pulp is fed behind a baffle at the shallow end, froth overflows the sides, and tailing is discharged through a pipe at the deep end of the cell.

Taggart<sup>(13)</sup> states that the capacity of a single cell is from 35 to 80 tons per 24 hr., air consumption from 6 to 12 cu. ft. of free air per minute per square foot of porous bottom at pressures of from 3 to 5 lb. per square inch.

Industrial objection to the Callow cell developed with the introduction of selective flotation and of coarser feeds. Use of Callow cells under modern circumstances results in blinding and corrosion of the blankets by pyritic and limy accumulations. This increases repair costs to the point where the inherent advantages of the Callow machine, namely simplicity and low first cost, are exceeded by the disadvantages. MacIntosh machines are replacing them.

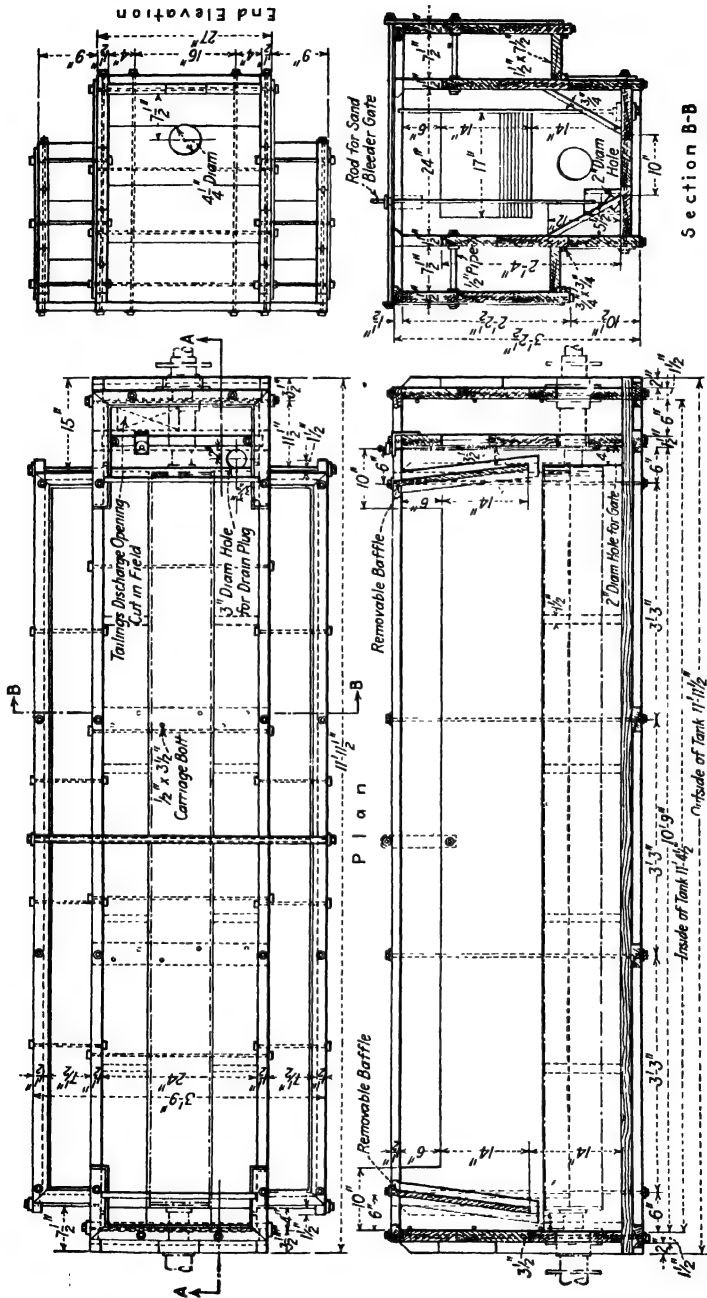


FIG. 110.—MacIntosh pneumatic machine. (The General Engineering Co.)

**Other Mat-type Pneumatic Machines.**—Several mat-type pneumatic cells have been built to suit special purposes, particularly to increase capacity per machine, therefore reduce attendance cost, and to decrease floor-space requirements. The Miami cell is typical.

The Inspiration cell (U. S. Patents 1,346,817/1920; 1,346,818/1920; and 1,401,598/1921) is similar to the Callow cell, except for the removable section of porous bottom (special concrete slabs) and lower slope which permits the construction of larger units.

**MacIntosh Rotating-mat Pneumatic Machine**<sup>(1)</sup>.—This machine (Fig. 110) consists of a truncated V-shaped trough in which a rotor revolves slowly. This rotor is covered with canvas socks through which air is blown under pressure, just as in Callow cells air is blown through the cell bottoms. To prevent sanding of the cell the rotor is fitted with a paddle extending about 2 in. from the surface. Feed enters one end behind a baffle; tailing leaves likewise at the other end. Froth overflows the sides of the machine in sloping troughs.

The principal advantage which is claimed for the machine is that pyrite and other "dropped" mineral particles do not permanently blind the canvas socks; this because of the rotation of the rotor which discharges sedimented particles half a revolution after their settling on the blankets. Interruptions for blanket repairs are minimized in duration by having on hand a few extra rotors fully soaked.

As compared with the Callow cell, the MacIntosh cell is more complicated and more expensive to build. But interruptions are less frequent and repair costs are lower. Metallurgical results are on a par.

The rotors are often directly driven by a small motor through speed reducers<sup>(8)</sup>.

*Mats for mat-pneumatic cells*<sup>(5)(10)</sup> may be made of canvas or palma twill, perforated rubber, lead shot, porous concrete, or rubber-impregnated canvas.

**Southwestern Flotation Machine.**—The Southwestern airlift matless pneumatic flotation machine (Fig. 111) is probably the simplest of all, yet it is the most recent in development. It consists of a wooden tank with semioctagonal bottom fitted with longitudinal baffles to regulate circulation, central vertical pipes equipped with regulating valves for gas introduction, a bell cover



over the pipe discharge to permit the establishment of quiescent, froth-separating zones on the two sides of the machine, and suitable launders for conveyance of the concentrate. Cross-partitioning of the machine to form short segments prevents by-passing of the pulp, which might otherwise occur, and simulates the conditions of units in series featured by agitation or sub-aeration machines.

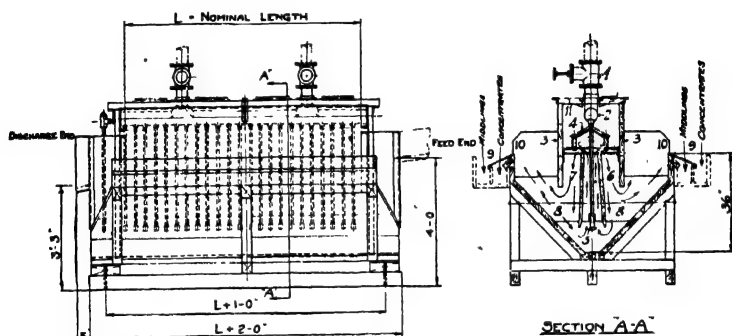


FIG. 111.—Southwestern matless air-lift machine. (*Southwestern Engineering Corp.*)

The cell was devised with minor variations by several metallurgists, particularly Forrester and Hunt. The patentees have consolidated their holdings and a single machine known as the Southwestern matless cell is available at the present time.

According to the makers, capacity ranges from 6 to 30 tons per foot of length of rougher machine per 24 hr. (Table 148.) Free-air requirement is 75 to 100 cu. ft. per linear foot of machine length per minute in roughing flotation and 45 to 70 for cleaning. Air pressure at the machine should approximate 1.7 lb. per square inch. Power required per linear foot of cell ranges from 0.3 to 1.0 hp., depending upon air requirements, blower efficiency, and frictional head loss in air mains.

The following advantages are claimed for Southwestern airlift cells:

- a. Low first cost.
- b. Low upkeep cost: few repairs, no moving parts.
- c. Low operating cost: low power requirements; little attendance.
- d. Simplicity of design and installation.

TABLE 148.—CAPACITY OF, SOUTHWESTERN FLOTATION MACHINES  
(Manufacturers' Data.)  
Specific gravity of ore, 2.70

Solids, per cent	Dry tons per 24 hr. per foot of rougher cell length*						
	Pulp specific gravity	Cubic feet per ton of pulp	Time contact in flotation cell				
			5 min.	10 min.	15 min.	20 min.	25 min.
15	1.114	29.0	14.8	7.4	4.9	3.9	2.9
20	1.144	28.0	20.6	10.3	6.8	5.1	4.1
25	1.187	27.0	26.6	13.3	8.8	6.6	5.3
30	1.233	26.0	33.2	16.6	11.0	8.3	6.6

Specific gravity of ore, 3.30

20	1.162	27.5	20.9	10.4	6.9	5.2	4.2
25	1.211	26.4	27.3	13.6	9.1	6.8	5.4
30	1.264	25.3	34.2	17.1	11.4	8.5	6.8
35	1.323	24.2	41.6	20.8	13.8	10.4	8.3
40	1.387	23.1	49.8	24.9	16.6	12.4	9.9

\* For estimating length of flotation machine required for 100 tons per 24 hr., or less, in the absence of metallurgical tests on the ore, it is advisable to allow a time contact of 15 to 20 min—although considerably greater capacities might be obtained after actual trial. Tabulation of cleaner flotation-cell capacities is omitted on account of the wide variation in operating conditions.

**Other Pneumatic Machines.**—The Cole (U. S. Patents 1,243,814/1917 and 1,375,200/1921) and Myers machines (U. S. Patent 1,323,373/1919) are among the more original of the various pneumatic machines that have been proposed.

**Comparison of Flotation Machines.**—In making a comparison between flotation machines, the following factors are involved: (a) metallurgical results, (b) first cost, (c) attendance, (d) power, (e) cost of auxiliary equipment necessitated by each type of machine, (f) floor space, (g) repairs and renewals, and (h) frequency and extent of shutdowns.

Generally speaking, agitation and sub-aeration machines make a lower tailing on extremely fine particles, in part because of finer air-in-water dispersion obtainable in them. On intermediate sizes, pneumatic machines make an equally satisfactory tailing. Sub-aeration machines are most easily controlled, pneumatic machines cheapest in first cost and power consumption.

Balancing all these factors, the difference between the various machines is small and cannot be ascertained with accuracy without a thorough testing campaign.

In recent years the trend has been toward sub-aeration and matless pneumatic machines.

#### AUXILIARY MACHINERY

**Conditioning tanks** are cylindrical or rectangular tanks fitted with a stirring mechanism designed to keep pulp in thorough suspension for an adjustable length of time. Pulp intake is by free discharge in the tank. Pulp outflow is from one of several holes in the side of the tank arranged at various heights to permit variations in conditioning time.

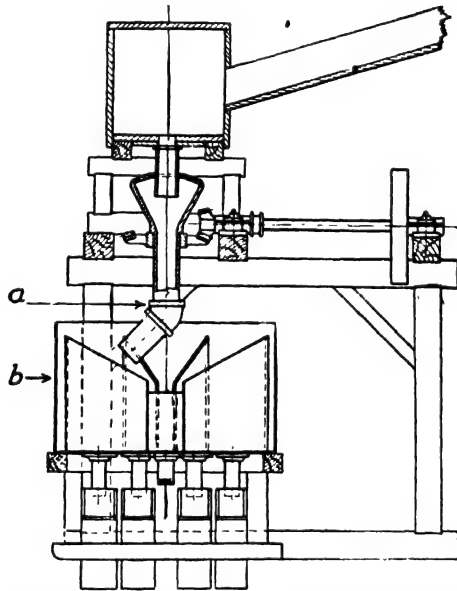


FIG. 112.—Pulp distributor. (*Allis Chalmers Co.*)

The pulp in conditioning tanks must be agitated sufficiently to keep the solids in suspension, but no more, as more vigorous agitation is needlessly costly and likely to result in the introduction of air, which may not be desired during conditioning.

Wooden tanks, preferably made of redwood, fitted with a paddle impeller running at 150 to 400 r.p.m. make satisfactory conditioning tanks.

Airlifts with a large well may be used as a combination conditioning tank and pulp elevator, particularly if oxidizing conditions are desired.

**Pulp Distributors.**—In small mills mechanical pulp distributors are generally dispensed with, the division of the pulp being made by forking a launder. Such an arrangement is not as accurate as the mechanical distributors installed in the better-equipped plants.

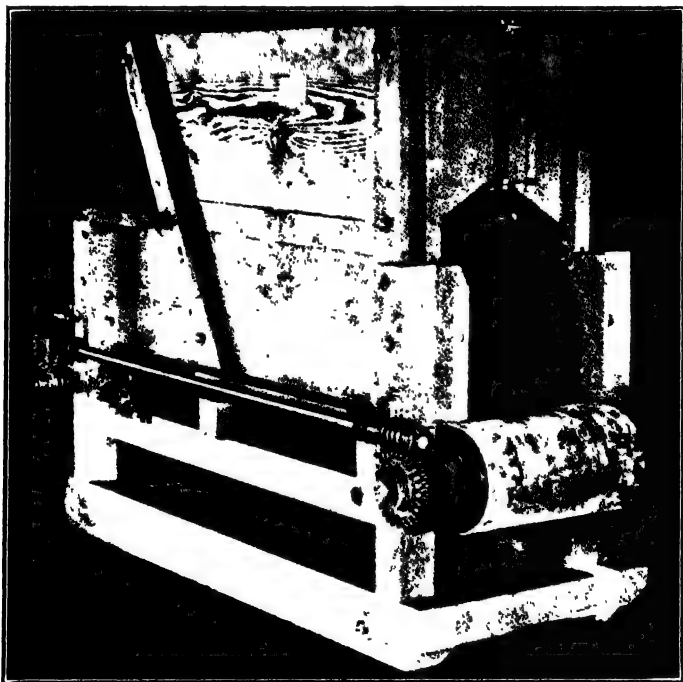


FIG. 113.—Belt-type, solid-reagent feeder. (*The Ruth Co.*)

Figure 112 shows a typical mechanical pulp distributor. It consists of a rotating inclined pipe *a* which receives the pulp to be distributed and pours into a compartmented tub *b*.

**Reagent Feeders.**—Reagent feeders are of several kinds, depending upon the type and amount of reagent to be fed.

Since reagents have to go in solution before acting in flotation (except certain froth-toughening oils) their introduction in the flotation circuit in aqueous solution is a distinct advantage. Highly water-soluble substances are easy to prepare in suitable

dilution for introduction in cells, unless they are used in large bulk; in that case it may be more economical to feed them in the solid state. Solid, difficultly soluble substances are fed dry in order to avoid the introduction of a large bulk of water in the pulp. Liquid, difficultly soluble substances are also fed directly.

Reagent feeders are classifiable into feeders for solid substances and feeders for liquid substances.

**Feeders for Solids.**—Slow-moving apron or belt conveyors are used for feeding lime, zinc sulfate, thiocarbamilid, soda ash, and copper sulfate.

For best results the solids must be ground finely in order to go in solution readily.

Solid-reagent feeders are not satisfactory unless the amount fed is large enough to fall in a constant stream from the end of the belt. To illustrate, suppose a solid were to be fed at the rate of 0.05 lb. per ton to the pulp entering a ball mill in a plant treating 25 tons of ore daily. This would be 0.05 lb. per hr. On a belt carrying a load 2 in. wide and  $\frac{1}{2}$  in. high, the speed required would be 2 to 6 in. per hour depending upon the fluffiness of the reagent. A belt traveling but  $\frac{1}{10}$  to  $\frac{1}{30}$  in. per minute is bound to feed irregularly.

Solid-reagent feeders must be easily adjustable as to speed or depth of bed on the feeding belt or apron so as to afford rapid control on pulp conditions.

Figure 113 illustrates a belt-type feeder.

**Feeders for Aqueous Solutions and Oils of Low Viscosity.**—Feeders of this type generally consist of a device whereby a known volume of liquid is scooped out of a reservoir at a known frequency. This gives intermittent feeding, but by proper adjustment of the frequency, of the volume of liquid, and of the conveyance of liquid from the feeder to the point of introduction in the pulp, the intermittence is so reduced that it is not objectionable.

A favorite feeder is shown in Fig. 114. It consists of rotating disks of fairly large diameter (1 to 2 ft.) on which are mounted a number of removable cups of identical capacity. These cups fill as they dip in the reservoir and are tripped to a known degree of emptiness by a special tripper. Adjustment of the tripper regulates the outflow per cup; adjustment of the number of cups and speed of main disk regulates the frequency of outflow. Adjustment can be made without interruption.

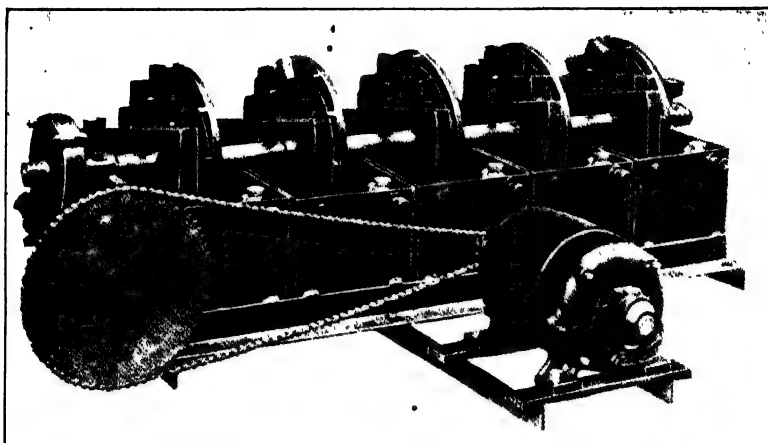


FIG. 114.—Cup-and-wheel reagent feeder. (*General Engineering Corp.*)

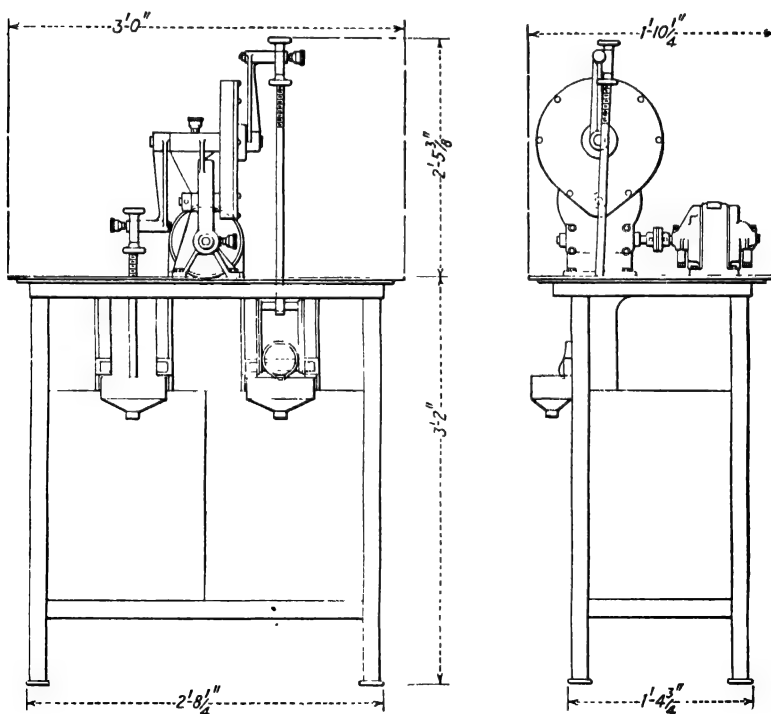


FIG. 115.—Geary reagent feeder. (*The Galigher Co.*)  
Two-cell unit.

The Geary feeder (Fig. 115) consists of a cup capable of vertical motion between guides, which is moved by a rod of adjustable length attached to a crank. At the top of its course the cup, which is slightly unbalanced and hinged at the bottom, pours its contents in a launder or pipe leading to the flotation circuit. This type of feeder, slightly modified, is being used to feed milk of lime as a substitute for a dry-lime feeder. Introduction of lime in milk-of-lime form is distinctly advantageous, as less time is required for thorough mixing and dissolving in the pulp.

Feeders for *viscous solutions* are based on the following principle: a film of liquid is picked up at the surface of a rotating disk plunging in the liquid and is scraped to a definite distance from the edge of the disk by means of a scraping edge. Adjustment is obtained by moving the scraping edge.

Feeders of this type are simple, but they suffer from irregularity in amount of material fed per unit time, due to changes in the viscosity of the oil with changes in temperature. They are being replaced by the more accurate tripping-cup types.

**Pulp-conveying Devices.**—Fine-pulp conveying devices consist principally of launders, pumps and piping, and airlifts.

Launders are rectangular, semicircular, or V-shaped troughs in which pulped solids are allowed to flow by gravity. The slope of launders depends on the size of the particles and on the viscosity of the flowing material. The coarser the particles and the more viscous the pulp, the steeper should be the launder.

TABLE 149.—AVERAGE LAUNDER SLOPES IN FLOTATION PLANTS  
Slope, Inches per Foot

Classifier Return to Grinding Mill	
Classifier set at 28 mesh	5 to 7
Classifier set at 65 mesh	3 to 5
Classifier set at 150 mesh	2 to 4
Classifier set at 300 mesh	1½ to 3
Mill Discharge	
Classifier set at 28 mesh	2½ to 4
Classifier set at 65 mesh	1½ to 2½
Classifier set at 150 mesh	1 to 2
Classifier set at 300 mesh	¾ to 1½
Classifier Overflow to Flotation	
Classifier set at 65 mesh	¾ to ¾
Classifier set at 150 mesh	¼ to ½
Classifier set at 300 mesh	⅓ to ⅔
Flotation concentrate	1½ to 3½
Flotation tailing	¼ to ¾

High viscosity is encountered in concentrate froths due to the presence of air bubbles. The viscosity of froths may be scores of times as large as that of tailing or feed pulps.

Table 149 gives desirable launder slopes for various mill products.

Sand pumps are used extensively for the elevation of flotation pulps. Figure 116 shows the Wilfley sand pump which is

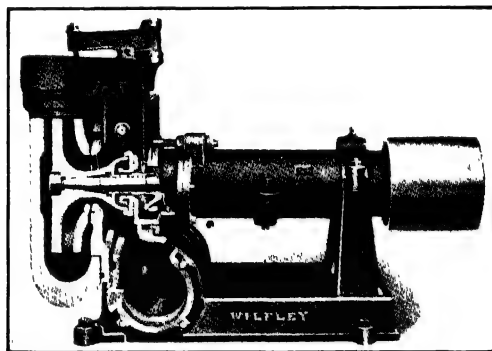


FIG. 116.—Wilfley sand pump. (A. R. Wilfley and Sons.)  
Sectional view.

eminently suited for the handling of flotation pulps. The Wilfley pump differs from the older style pumps by the use of a centrifugal seal in place of a stuffing box to prevent leakage. The centrifugal seal consists of (a) a revolving member or expeller having wings or paddles radiating from a recess in its center to its periphery, and (b) a stationary member that has a projecting groove. The revolving member is set close to the stationary member which acts as a side-wearing plate. In action, the material is prevented from leaking out by the centrifugal action of the wings of the expeller, and any slippage by the side is caught by the projecting groove and delivered to the wings. An automatic check valve seals the shaft while the pump is not in operation. The pump is so constructed as to permit quick opening for repairs and replacement of worn parts.

Airlifts are used in some installations for the elevation of pulps. Their use is naturally restricted to plants having compressed air already available.

**Air Supply.**—Pneumatic machines and some sub-aeration machines require air in large bulk and at low pressure. This is supplied by blowers such as the Roots cycloidal blower.



**Thickeners.**—Two types of thickeners have been adopted for dewatering flotation pulps, one of which is a thickener proper and the other a filter thickener.

The Dorr thickener depends for its operation on consolidation settling of flocculated pulps. It consists of a cylindrical tank of large area whose bottom is scraped toward the center by a raking mechanism rotating at low speed. The thickened sludge



FIG. 117.—American disk filter in operation. (*United-Oliver Filters Co.*)  
This filter dewateres a lead concentrate (left) and a zinc concentrate (right). Accordingly, the pulp tank is divided into two parts.

is discharged by a diaphragm pump. Clear solution overflows at the top of the thickener. The operation is continuous.

The Genter, Hardinge, and Hydrotator thickeners are essentially filter thickeners. In the Genter type<sup>(4)</sup>, filtering leaves actuated much as those of a continuous vacuum-pressure filter are submerged in the thickener tank and abstract solution, thus thickening the pulp. In the Hardinge and Hydrotator thick-

eners consolidation settling of flocculated pulps is accompanied by filtration through a sand bed.

**Filters.**—Vacuum filters are used exclusively for the final dewatering of flotation concentrates. The filters are of three types: (a) drum-type filtering on outside, (b) leaf-type, and (c) drum-type filtering on inside.

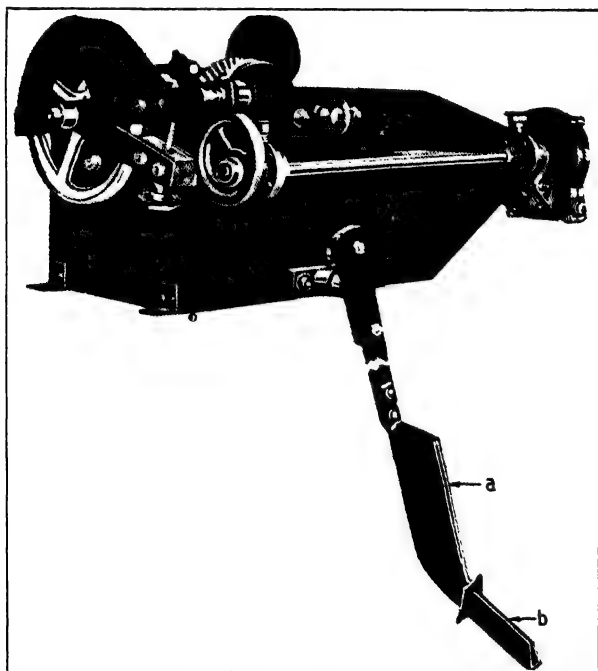


FIG. 118.—Pulp sampler. (*The General Engineering Co.*)

All three types are characterized by continuous operation of the machine as a whole, but by the alternating suction and pressure applied to the filtering medium. Suction results in forming a cake of solids at the surface of the filtering cloth, and pressure blows the cake away from the surface.

Drum-type filters with outside filtering surface are typified by the Oliver filter, disk filters by the American filter (Fig. 117), and drum filters with inside filtering surface by the Dorco filter.

Centrifugal filters are used in some collieries.

**Pulp Samplers**<sup>(6)</sup>.—Several types of pulp samplers have been devised. Figure 118 shows the Auto Sampler of the General

Engineering Company. It consists essentially of a cutter *a*, which deflects a portion of a freely falling pulp stream into a cutter boot *b*, thence into a sample launder. In operation the cutter moves at constant speed across the pulp stream. The

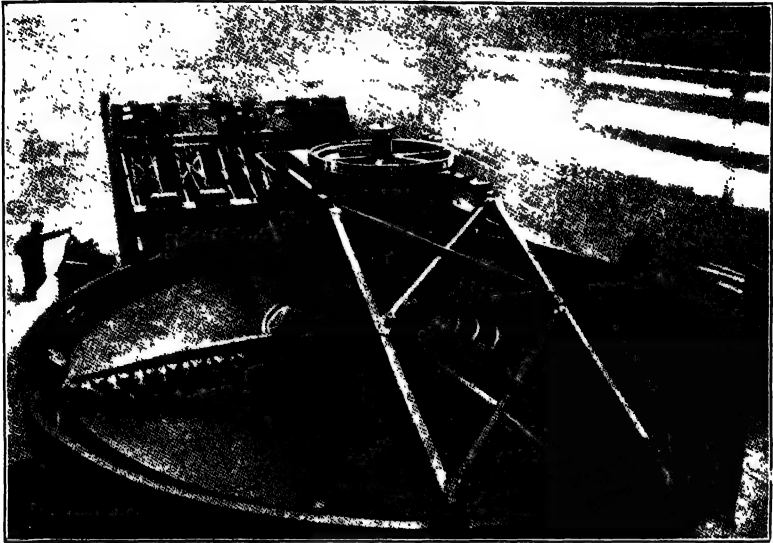


FIG. 119.—Large bowl classifier. (*The Dorr Co.*)

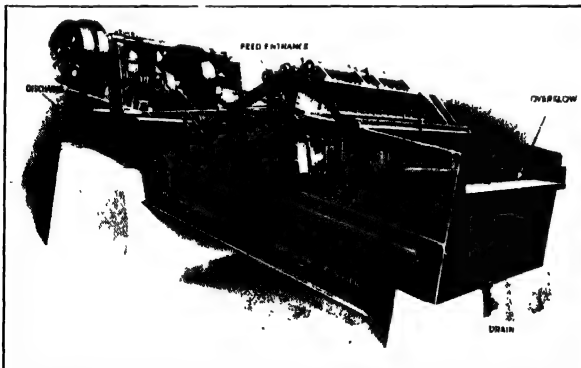


FIG. 120.—Rake classifier. (*The Dorr Co.*)

sampler is provided with a timing device which brings about the cutting of a sample at regular and adjustable time intervals.

**Grinding Mills and Classifiers.**—Two principal types of grinding mills are in general use. They are the cylindrical mills and

cylindro-conical mill. Much ink has been used in debating their relative merits. So far, they are still in competition and therefore substantially equivalent in nearly all instances.

Classifiers are of two principal types: the so-called hydraulic classifiers involving settling of solids against a rising current of liquid, and the so-called mechanical classifiers involving sedimentation of solids together with scraping of the sediment into an inclined sand elevator. Mechanical classifiers hold the field of classification in connection with flotation. The Dorr bowl classifier (Fig. 119) is typical of the machines used for fine sizing, and the standard Dorr rake classifier (Fig. 120) and Akins spiral-ribbon classifier for coarser sizing.

## CHAPTER XV

### SOME POINTERS ON MILL DESIGN

The design of flotation plants involves certain factors common to the design of all ore-dressing plants, as well as certain special factors that derive from the exacting physicochemical requirements of the process. Those factors common to ore-dressing plants in general will be treated in a cursory manner, but special emphasis will be placed on those factors that derive from the use of flotation.

#### PLANT CAPACITY •

**Milling Considerations.**—The capacity of an ore-treatment plant should be determined from the extent of ore reserves, nature of deposit, and financial resources of the individuals or company interested in its erection. Generally speaking, a larger plant costs less per unit daily capacity, operating costs are lower per ton treated, and metallurgical results are slightly better. On the other hand, a larger plant for a given deposit necessitates higher amortization charges. If adequate financial resources are available, if sufficiently definite knowledge of the ore reserves is at hand, and if the desirability of treating an ore has been proved metallurgically and economically, the problem of determining best plant capacity is reduced to a balance between the items of initial cost, operating cost, metallurgical results, and amortization charges. Solution of such a problem can be obtained by trial and error. The following is an illustration.

An ore body has been blocked out, containing approximately 730,000 tons of ore. Flotation plants ranging in daily capacity from 100 to 2000 tons are considered. Suppose that it is known that first cost is \$900 per ton daily capacity for a 100-ton plant, \$800, \$700, and \$600, respectively, for 400-ton, 1000-ton, and 2000-ton plants. Assume also operating cost per ton of \$1.75 for the 100-ton plant, \$1.25, \$1.00, \$0.75, and \$0.60, respectively, for 200-ton, 400-ton, 1000-ton, and 2000-ton plants. Interest

at 5 per cent. Recovery and grade of concentrate identical in all cases.

Estimation of correct plant capacity may be made from a tabulation such as is presented in Table 150.

TABLE 150.—DETERMINATION OF MOST ECONOMICAL PLANT CAPACITY FOR THE TREATMENT OF A GIVEN ORE

Cost division	Plant capacity, tons per day							
	100	150	200	300	400	600	1000	2000
Life of plant, years . . . . .	20	13.3	10	6.7	5	3.3	2	1
Plant cost per ton daily capacity, dollars . . . . .	900	875	850	825	800	750	700	600
Total plant cost (000 omitted), dollars . . . . .	90	131	170	247	320	450	700	1200
Depreciation and obsolescence, per ton treated, dollars*	0.12	0.18	0.23	0.34	0.44	0.62	0.96	1.64
Interest on investment, per ton, dollars . . . . .	0.13	0.12	0.12	0.11	0.11	0.10	0.09	0.08
Operating cost, per ton, dollars	1.75	1.50	1.25	1.12	1.00	0.87	0.75	0.60
Total cost, per ton, dollars	2.00	1.80	1.60	1.57	1.55	1.59	1.80	2.22

Table 150 shows that a 400-ton plant would be most economical when the problem is viewed from a milling standpoint only. But in arriving at a decision concerning the plant capacity needed in the treatment of an ore deposit other considerations than milling enter. Foremost are mining, transportation, marketing, and financial matters.

**Mining Considerations.**—As the type of mining operation that can be used is controlled essentially by the nature of the deposit, the operating cost of mining decreases less sharply with capacity than the operating cost of flotation. Other considerations in respect to the total mining cost are similar to those involved in milling operations. The net result, so far as mining considerations are concerned, generally indicates a somewhat longer economic life than is indicated by milling.

**Transportation Considerations<sup>(1)</sup>.**—Transportation costs, if the service can be purchased from an existing concern, are relatively independent of the amount shipped, although a slight reduction can be obtained for bulkier even though shorter lived shipments. If transportation is to be supplied by the mining and milling enterprise and the equipment is to be scrapped after exhaustion

of the deposit, some intermediate duration of the operations is generally most economical.

Concordance of this most economical scale of operations from a transportation standpoint with the most economical scale of operations from a milling standpoint is not always obtained as the general conditions and ore reserves may indicate different means of transportation: truck, cableway, railroad, or conveyor-belt transportation may be most economical.

Trucks are suitable for the shortest lived operations and railroads for the longest, trucks for the smallest scale and conveyors for the largest scale, railroads or trucks for the long hauls, cableways or conveyors for the short hauls. Topography is an added factor which often controls the choice of transportation means, *e.g.*, cableways and conveyors are suitable for the most rugged topography, and railroads for the most level.

**Marketing and Financial Considerations.**—Marketing sometimes commands restriction of output either because freight charges to distant and competitive markets are prohibitive or because world consumption is small. Small world consumption connotes high susceptibility of market price to fluctuations in output.

Financial resources of operating companies or individuals frequently compel building a plant somewhat smaller than that appearing to be the most economical from technological considerations: it is best to err conservatively.

**Summary.**—Analysis of the problem indicates in most instances a most desirable mill life of 5 to 30 years. Small deposits are usually most efficiently treated on the basis of a short life, and large deposits of a long one. Very large deposits will no doubt be treated for periods of time larger than 30 years, partly because of the development of bulky ore reserves of lower grade following the introduction of operating economies, and partly because of the development of more effective treatment methods.

## LOCATION

**General.**—Choice of mill location is influenced by the mine location, smelter (or market) location, transportation facilities, water supply, tailing disposal, and labor supply.

If mine and smelter are not near each other it is best to locate the mill at the mine, as transportation charges are thus applied

to the relatively small bulk of concentrate instead of to the large bulk of raw ore. Location of the concentrator at the smelter presents certain minor advantages of which availability of water and labor, lessened cost of supervision, and possibility for closer personnel cooperation are the most common.

Location of the mill at an intermediate point between mine and smelter is expedient if existing transportation facilities, or area for tailing disposal or water supply, dictate. For instance, if a mine is located high on a mountain side where water is not available it may be necessary to place the mill at the base of the mountain rather than to pump water from a stream to the mine.

In the case of some of the larger plants having a higher life expectancy than smaller mills, tailing disposal becomes of paramount importance in view of the large area required for that purpose. Labor considerations also are of importance.

In general, small mines are relatively distant from smelters, and mills for the concentration of their ores are erected at the mine. In the case of large ore deposits a smelter is often built to treat the concentrates as near the mine as is economically feasible. In those cases the mills are located at the smelter if the factors that favor location at the smelter outweigh the cost of hauling waste.

**Mill Site.**—Three types of mill sites are in use: (a) on sloping ground, (b) on flat ground, and (c) on partly inclined and partly flat ground.

Mill sites on inclined ground of the proper slope (about 20 deg.) have the advantage that gravity flow can be used for the conveyance of material from one dressing step to another. Also, a larger proportion of the machines can be placed directly on the ground and since sloping ground is frequently rocky, a better foundation is obtained.

Mill sites on flat ground are more compact and the building is less expensive per cubic foot of available space.

The advantage of sloping plants over plants built on flat ground is less for flotation than for gravity concentration, as flow-sheets are relatively simpler, requiring fewer conveying steps, and as fine pulps are conveyed and elevated easily by pumps. Pumping is inexpensive and permits a greater flexibility in plant arrangement than is obtainable by a combination of launders and elevators.

Mill sites on partly inclined and partly flat ground are especially suited to flotation treatment, the sloping ground being used to



support the coarse-crushing and intermediate-crushing divisions, and the flat ground the fine-grinding and flotation divisions<sup>(s)</sup>.

### WATER SUPPLY

Securing water is frequently one of the main difficulties facing the establishment of a new flotation plant. In some instances, indeed, the lack of adequate water or water rights has been of prime importance in determining the type of ore treatment or in causing the sale of the ore to a competing organization.

Adequate water supply implies not only a sufficiency of water, but also certain requirements as to quality.

**Quantity.**—The quantity of water required is smaller for flotation than for gravity concentration. As a rule, the pulp in flotation cells contains from 18 to 35 per cent solids, indicating a water consumption in pulp making of 4.8 to 1.8 tons for each ton of ore treated. Incidental water consumption, such as for concentrate flushing, raises the consumption to a total of from 2 to 5 tons per ton of ore.

Water consumption can be reduced by re-using the water held by the wet concentrates and tailing. Thickeners and filters reduce the water content of concentrates to about 10 per cent. Thickeners or tailing dams can reduce the water content of tailings to from 35 to 50 per cent, depending on the character of the pulp. Accordingly, the water consumption can be reduced to from three-quarters to one ton per ton of ore, if water reclamation is practiced.

**Quality.**—Inasmuch as many salts and organic substances have a marked effect on flotation operation<sup>(s)</sup>, it is desirable to use water that does not contain soluble salts other than those whose presence is known to be desirable or harmless.

The available water may be lake or stream water, mine water, salt-lake or sea water. Since the available water contains suspended solids or dissolved impurities, or both, water treatment is often necessary.

The quality of the water may be improved through "softening" or similar treatments mainly designed to remove the dissolved impurities. Usually suspended impurities are in too small quantity to have much effect. They occur, of course, in swift-moving streams but are inconsequential in lake or sea water, due to the settling opportunities that have been afforded. In case

the suspended solids are objectionable they can be removed through the use of settling ponds.

Dissolved impurities in mill water are far more important than suspended impurities. They are derived from atmospheric, organic, and mineral sources<sup>(2)</sup>.

The atmosphere supplies gases in various concentrations, and particularly oxygen and carbon dioxide which take part in reactions of great importance. Oxygen and carbon dioxide being more soluble in water than nitrogen and the other gases of the atmosphere, their concentration in water is relatively larger.

Little is known concerning the action of organic impurities because of the multiplicity of organic decay substances, of their low concentration, and of the difficulty in analyzing for them. The great influence of such substances as tannic acid, glue, starch, gelatin, on the flotation of most minerals, makes it desirable to get water that is free from organic contamination. Impurities of organic origin are most likely in waters that have percolated through marshy or woody country, that is where the slope of the ground is small and where a thick coating of detrital matter and of soil covers the rock. A large amount of rainfall acts as a diluent and prevents the development of poisonous concentrations of decay impurities.

**Soluble Salts in Natural Waters.**--The solid content dissolved in natural waters varies greatly according to the type of water, the character of the subjacent rock, vegetation, and climate. The most common inorganic substances are carbonates (as such or as bicarbonates), sulfates and chlorides of calcium, magnesium and sodium, together with silica.

The total salinity of rivers and lakes<sup>(2)</sup> varies from 50 to 300 parts per million (p.p.m.). If average river water is used to pulp an ore in the ratio of 3 parts of water to 1 part of solid, the salinity of the pulp derived from the water is equivalent to 0.3 to 1.8 lb. per ton of solid. This quantity of soluble salts is not necessarily significant of important effects in flotation, but it should be kept in mind that it is of the same order of magnitude as customary reagent additions. In many mountain regions, particularly if igneous rocks are abundant, the salinity of stream water is less than average, 20 to 100 p.p.m. being the usual range. In industrial regions, and where streams are slow-moving, greater salt concentrations are common.

The most abundant anion is the carbonate ion (including the bicarbonate ion); it is derived both from the dissolution of carbonate rocks and from solution of atmospheric carbon dioxide. In regions of igneous rocks (such as in many metal-mining regions) it is not so important a constituent of surface waters as in regions where the subsoil is of sedimentary origin. The next most abundant anion is the sulfate ion; it is derived from the dissolution of gypsum and the oxidation of sulfides. In mining regions the sulfate ion is frequently the commonest anion of surface water.

The most abundant cation is the calcium ion which is derived from limestones, many sedimentary rocks, and a number of igneous rocks. Magnesium and sodium are also common.

**Soluble Salts in Mine Waters.**—Due to the natural concentration of exceptional minerals in mines, mine waters differ considerably from surface waters. The sulfate ion is the most abundant of all the anions. It is derived from the oxidation of sulfides. Common cations are zinc, iron, copper, and hydrogen. Mine waters are frequently acid in contrast to surface waters which are alkaline or neutral.

Mine waters sometimes contain considerable colloidal ferric hydroxide and some colloidal alumina.

**Soluble Salts in Ores.**—Besides the mineral impurities contained in the water used in pulping the ore, a large amount of soluble salts is added to the pulp by the ore itself. The most abundant soluble salts provided by sulfide ores are sulfates.

Iron sulfates have oxygen-carrying qualities, the change from the ferric to the ferrous condition being a reversible process. Some solid surfaces reduce ferric ion; other surfaces or dissolved oxygen may oxidize ferrous ion, making it possible for iron salts to be oxidized in one place and reduced in another within the body of a pulp. Iron salts may thus complete a cycle whereby one substance is oxidized and another reduced. If such circumstances prevail, iron sulfates are truly oxidation (or reduction) catalysts, and their presence, even in small concentration, may have large effects. Besides, iron salts are acid salts and impart to the pulp a pH that is not desirable for selective sulfide flotation. Lime, caustic soda, alkaline salts, such as soda ash or trisodium phosphate, are used to precipitate the iron as hydroxide or basic sulfate.

Copper sulfate is the standard activator for sphalerite and should therefore be removed from the pulp during the lead-

floating cycle of lead-zinc selective flotation operations and during the copper-floating cycle of copper-zinc operations. It is not possible to cause this removal before some reaction between the copper sulfate and the surface of the zinc-sulfide particles has taken place. The decopperizing of selective flotation pulps is therefore carried on, during the same time in which the zinc-sulfide surfaces are cleansed, through the use of cyanides or other reagents. The presence of soluble zinc salts in lead-zinc-iron ores favors the removal of copper-sulfide coatings from sphalerite surfaces because the zinc ions stand ready to take the place of copper atoms at the surface of the sphalerite when these copper atoms are taken up into undissociated complex ions.

The comparatively non-reactive soluble content of ores is not difficult to determine but the same is not true of the reactive content. This is because of the rapid disappearance, by reaction, of the all-important soluble salts, even before an analysis can be started.

An interesting study was made by C. G. McLachlan of the effect of soluble salts in flotation<sup>(6)</sup>. Although his conclusion is negative concerning the detrimental effect of soluble salts on the Nacozari ore, it need not invalidate the general suspicion with which unknown soluble ingredients of mill waters are generally regarded.

**Correction of Mill Water.**—The most objectionable feature of the water supplied to many mills is that the hydrogen-ion concentration is not the same as that at which flotation is most efficiently carried out. The adjustment of the mill water to the proper pH is readily made through the addition of acid or alkaline reagents; pH adjustment is becoming the largest item in the cost of reagents for sulfide flotation.

Reagents added in order to adjust the pH have a threefold use: (a) they react with dissolved salts or gases, (b) they react with mineral surfaces, and (c) they change the pH. Consumption of alkaline reagents by reaction with dissolved salts may be a particularly large item; it is, therefore, desirable to select carefully the water to be used in pulping the ore wherever such choice is possible.

**Variations in Water.**—Water from a large supply such as a lake is very uniform in composition. But stream water, particularly in mountain regions where streams flow rapidly, changes suddenly in composition with changes in rainfall, as well as seasonally.

The spring thaw in regions of marked seasonal changes is accompanied by an increase in soluble salts, as the products of winter weathering are carried off. Mine water is likely to change suddenly in character with the occasional inflow of water from new sources of supply as development and mining proceed.

**Salts in Reclaimed Water.**—Accumulation of certain salts takes place in reclaimed water. This is especially true of the salts which are supplied by the ore and, generally, of constituents that are harmless in low concentration. Accumulation may, of course, make these constituents objectionable.

Besides circuit water differs from fresh water in that it contains a small residual amount of inorganic agents—as likewise frothing agents to an extent almost sufficient to sustain flotation. In plants reclaiming water, the frothing-agent requirement is much smaller than in plants using fresh water exclusively.

Water reclamation is generally more expensive than the economy in water and reagents resulting from its use. It is employed only if it is urgent to save water.

**Storage of Water.**—The most satisfactory arrangement consists in providing a reservoir at a higher level than the mill in order to allow the water to flow by gravity. Such a reservoir may be a natural lake or an artificial body of water obtained by damming a stream. Flow to the mill generally is through a wooden flume, but pipe is economical if the requirements are small. A rapid flow of water is sufficient to prevent freezing, but if flow is interrupted freezing may set in.

Pumping from a stream at a lower level to a small tank at the highest point in the mill is another method of bringing water to the plant. This is more expensive and is more likely to become interrupted than the gravity-flow method. In plants regenerating water, pumping has to be employed extensively. It accounts for a good share of the expense of water reclamation.

**Impurities in Tailing Water.**—It has been asserted that the water discharged from some flotation plants is so polluted as to harm plant and animal life. Although it is true that streams receiving tailing pulps or water from tailing dams are made turbid by fine suspended solids, there is no evidence that cyanide, for instance, persists as such in the tailing water. Other reagents added in flotation plants are substantially innocuous to life and can hardly be construed as the cause of much damage.

**Water Heating.**—In some plants it is customary to warm the pulp to 30°C. (or warmer) ahead of zinc flotation, or as a step in cleaning zinc concentrates. This can be done by blowing live or spent steam in flotation cells or conditioning tanks.

### TAILING DISPOSAL

Since the bulk of the ore concentrated by flotation appears in the tailing, considerable care must be exercised in securing space for its disposal.

For instance, a mill treating 1000 tons of ore per day and having an anticipated life of 15 years will produce in the course of its life some 4,000,000 tons of tailing occupying a volume of 2,000,000 or 3,000,000 cubic yards. Since flotation tailing is fine, it cannot be stacked to great height, but rather must be allowed to flow in thin sheets whose spreading is stopped by a dam.

If a tailing is discarded without substantial damming the deposit will take the form of a very flat cone whose slope approximates that of a launder in which the pulp will just flow. In such a case a large area is necessary. This method is inexpensive and recommendable in arid country where land is cheap.

However, impounding tailings is generally practiced as it limits the area required, allows reclamation of the water, and makes the eventual retreatment of the tailings easier. A tailing can be impounded by building a dam of stone, concrete, or earth against which the pulp settles, or cheaper still, by allowing the sandy portion of the tailing to build it; the last alternative is general. It involves classifying the pulp into sand and slime. The sand builds the dam which is made impervious by slime filling the pores between the sand particles. The body of the slime flocculates and settles behind the dam.

At Inspiration, desliming cones located at the tailing dam separate the pulp into sand and slime; a sand bar 40 ft. high is deposited as damming material, and the slime consolidates behind.

According to W. L. Zeigler<sup>(s)</sup> a satisfactory and simple method of impounding tailings is as shown in Fig. 121. The pulp is distributed along the spout *A*, the sand settling directly and the slime being carried in the pond area *B* where it settles after flocculating. Sand is shoveled either continuously or at intervals to form a bank somewhat higher than the level of the water which is withdrawn clear of solids by flume *C*. When the level

of the flocculated pulp and artificial sand bar has risen so as to make tailing discharge and shoveling difficult, the spouted flume is moved to a higher position farther upstream and the water-discharging flume *C* is lengthened.

Flotation tailing piles give rise to dust storms in dry, windy weather. Whenever possible the tailing should be placed so as to be blown by the prevailing winds away from neighboring cities or towns. The metal content of tailings (particularly

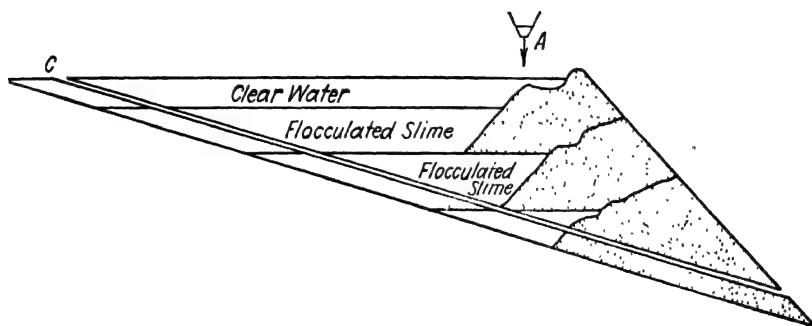


FIG. 121.—Diagrammatic section of tailing dam and impounding. (After Zeigler.)

copper) prevents plant growth, so that tailing piles are and remain unsightly. Esthetic considerations demand that they be laid out so as not to be the most obvious feature in the landscape.

Because elevating a bulky waste product diluted with much water is expensive, an important consideration in choosing an area for tailing disposal is to locate the mill so that gravity flow to the tailing pond is possible.

Disposal of tailing as mine filling is sometimes possible. It is practiced in districts in which the ore deposits are of suitable character. In the Butte District fine tailing is flumed at low cost in burning zones to extinguish mine fires.

#### MILL ARRANGEMENT<sup>(4)</sup>

**Crushing and Storing.**—Crushing machinery can operate with large load variations in a short time; intermittence in operation is of no material consequence. But continuity and evenness of operation are desirable for the fine-grinding and classifying operations and still more for flotation. Accordingly, a storage bin ahead of the fine-grinding division is necessary. A bin ahead of coarse crushing is merely an unloading and feeding

convenience and its capacity need not be as large as that of the bin separating crushing from grinding.

In view of the large capacity available per dollar invested in coarse-crushing machinery as compared with grinding machinery, and of the relatively large labor attendance for crushers, crushing is most economically conducted during one or two 8-hr. shifts although the rest of the mill operates on three shifts. The crushing division should therefore have a continuous-rating capacity three times (or one and a half times) as large as the other divisions of the plant. Duplication, in the coarse-crushing plant, of those units whose repairs might call for several days' delay is a wise investment. Modern design provides for the installation of one spare crusher for each coarse crushing stage.

The storage bin for crushed ore should have a capacity sufficient to take care of the one- or two-shift daily shutdown of the crushing plant. The strict minimum is therefore 8- or 16-hr. supply, that is one-third or two-thirds of the daily plant capacity. In view of variations in mine output, and for the purpose of feeding a more uniform material to the grinding section, a substantially larger capacity is desirable. In many foreign countries and in some American mining camps no mining is done on Sundays or holidays, but the mill is operated continuously. In those instances a bin capacity of  $1\frac{2}{3}$  days is the minimum. If bin capacity is near the minimum, systematic fluctuations in metal content are likely to occur from shift to shift. This arises from the fact that ore particles segregate in the bin, coarse particles accumulating in one portion and fine particles in another; when the crushed ore is withdrawn, variations in the character of the ore stream are inevitable. To minimize these variations and to provide for unusual contingencies, fine-ore bins are generally designed with enough capacity to supply the fine-grinding and flotation divisions for two or three days.

**Grinding.**—Fine grinders need not be available with such a surplus capacity as coarse crushers because fine grinding is usually performed in several units in parallel, and that if one unit is out of commission the rest can perform as usual. Also, accidents to ball or rod mills are rarer than to crushers. They have to be relined, it is true, but interruptions from that cause recur at regular intervals and repairs can be made somewhat more at the convenience of the operator.



Up to recently it was considered best to arrange ball mills with the classifiers in circuit with them side by side so that the discharge from the mill could feed by gravity to the classifiers, and the classifier sand return likewise to the mill. This is still considered the best arrangement for small installations. But in the case of large plants practice has drifted away from this arrangement, possibly because it is not flexible or suited to the increased classifier capacity that is being provided for a given fine-grinding capacity. Instead, the classifiers are placed on a floor above the mills, so as to crowd the latter on a smaller ground-floor space and so as to provide gravity flow from the classifiers to the flotation sections. Mill discharge is pumped or elevated to the classifiers.

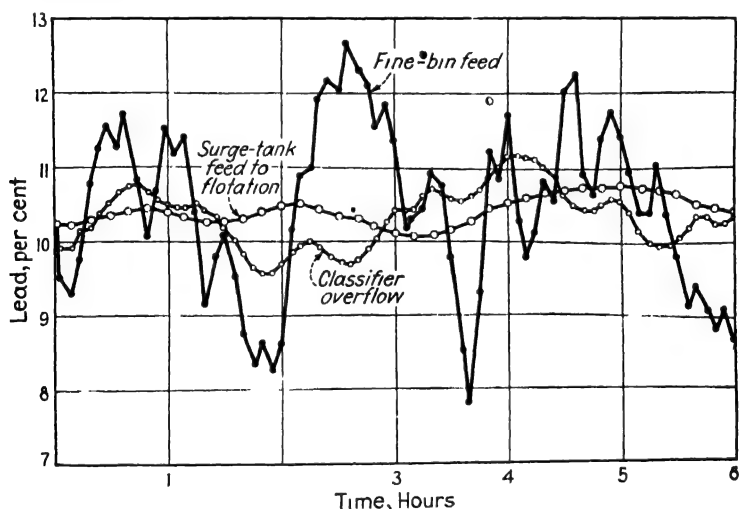


FIG. 122.—Fluctuations in feed assay in flotation plant treating spotty lead ore.

**Flotation.**—Smooth operation of the flotation division and the production of satisfactory metallurgical results are dependent on the uniformity of the feed pulp. Uniformity in particle size is generally well attained by controlling fine grinding with a classifier in closed circuit. Uniformity in grade and tonnage are more difficult to obtain. Uniform grade is not obtained in the crusher feed of most mills because of the spotty character of the ore. Fortunately, considerable dampening in the amplitude of the grade variations results from the mixing action in the bins, mills, and classifiers, so that a great reduction may be noticed

in the variations in instantaneous metal content of the ore stream in going from the crushing to the flotation division (Fig. 122). Further improvement can be had through the use of surge tanks in which the pulp experiences a substantial delay.

In the flotation division a reserve capacity of about 25 per cent over that needed for operation under normal conditions is ample. This can be cut down if surge tanks are used as they reduce the amplitude of feed variations over short periods of time. When not directly employed, reserve capacity is used for scavenging purposes, a number of cells (or pans) toward the tailing-discharge end being allowed to well rather freely, producing a low-grade middling for further treatment.

**Surge Tanks.**—Surge tanks should be large enough to hold in storage enough pulp to keep the flotation division going for  $\frac{1}{2}$  to 2 hr. For each ton daily capacity, and 1 hr. storage, tank capacity should be

$$\left(n + \frac{1}{D}\right) \times \frac{1}{24} \times \frac{2000}{8.34} \text{ or } 10\left(n + \frac{1}{D}\right) \text{ gallons,}$$

in which  $n$  is the pulp dilution (tons of water per ton of ore) and  $D$  the density of the ore. For average conditions ( $n = 3$ ,  $D = 3$ ) and 2-hr. storage, a tank capacity of 66 gal. per ton of daily mill capacity is required.

Surge tanks are not so necessary in plants handling a large tonnage of ore because variations in grade are less ample with increase in tonnage. Statistical analysis suggests that, other things being equal, the amplitude in grade variations of the feed to a mill should vary inversely as the square root of the tonnage. For small plants surge tanks are a means for keeping operations going smoothly, hence efficiently. Also, their first cost is small: for a 100-ton plant treating a 3:1 pulp of an ore of density 3.0, a surge tank providing 2-hr. storage should have a volume of 890 cu. ft. This is amply provided by a cylindrical tank 12 ft. in diameter and 10 ft. high.

**Scavenging Operations.**—The practice of using scavenger flotation cells which are allowed to overflow freely during flotation throws the bulk of the variations into the scavenger concentrate. In this way, the irregularities of grade and tonnage are concentrated in that circuit which needs therefore considerable attention (Fig. 123). Since the scavenger concentrate is generally returned to the head of the rougher cells together with a variable cleaner tailing (Fig. 124), considerable variation in the grade

and tonnage fed to the roughers is induced. Here again a surge tank serves a useful purpose in spreading over a substantial time the variations in tonnage and grade of the products returned to the roughers.

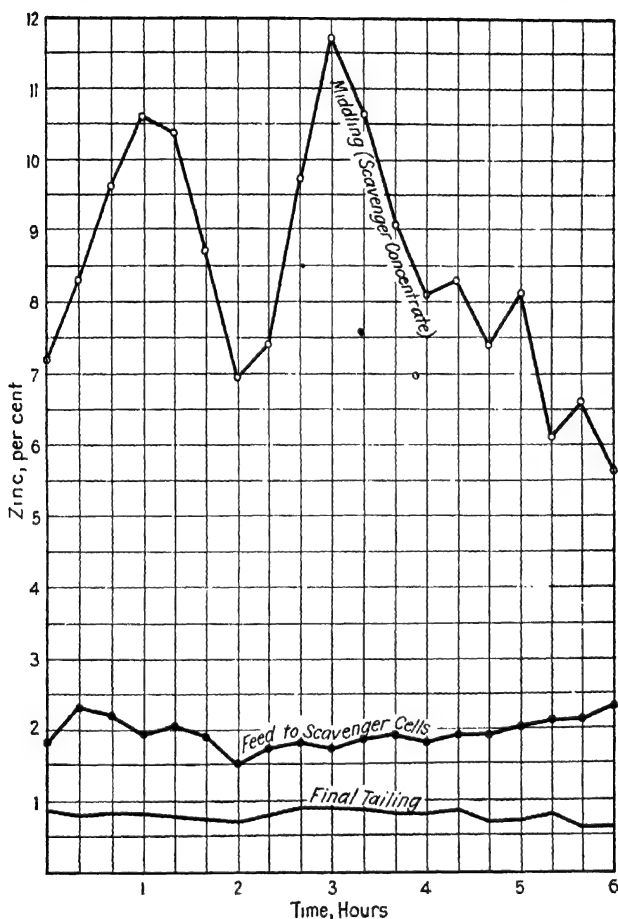


FIG. 123.—Fluctuations in zinc grade of scavenger-cell products at selective flotation plant.

**Miscellaneous Features.**—The use of thickeners to separate from each other the circuits in which different metals are floated in selective flotation plants would make possible the employment of circuits at a pH or salt concentration more nearly suited to

each operation. So far, however, circuits of this type have not been used.

In some modern plants a complex system of pumps has been installed to take care of spills. At Midvale<sup>(3)</sup> (Fig. 125) the floor is divided by concrete partitions a few inches high. The purpose of the partitions is to segregate the spills from various

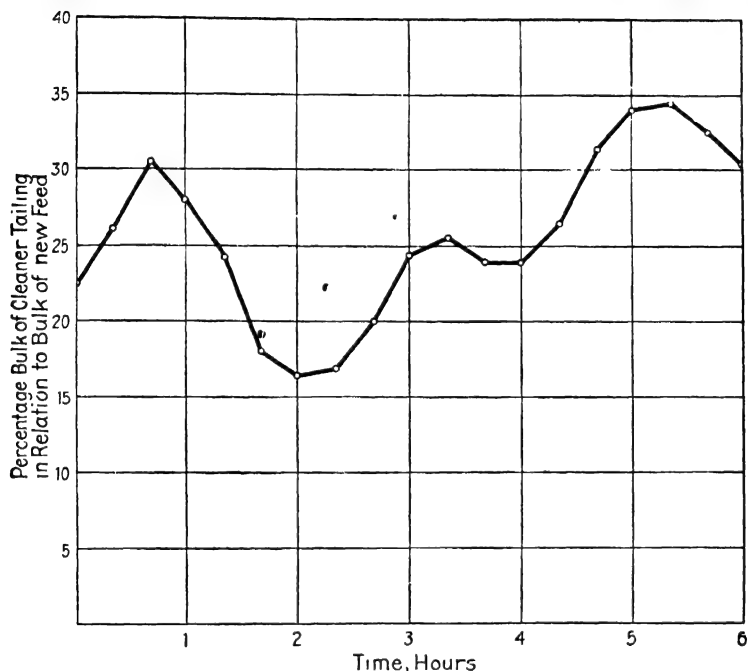


FIG. 124.—Fluctuations in relative bulk of cleaner tailing and new feed in copper flotation plant.

places into several pump wells, so as to permit return of the spills at the proper place in the circuits.

Pilot tables have been installed at certain mills to inspect the products made by flotation. In other plants the equivalent inspection is made by intermittent hand vanning. Pilot tables should be well lighted for efficient usage. Mercury-vapor lamps have been used to advantage for vanning, as some color contrasts (*e.g.*, of galena to sphalerite) are more striking in blue light than in daylight.

Reagent mixing tanks for the addition of reagents in solution, reagent storage tanks, and reagent bins should be placed so as to feed by gravity to the point of introduction in the circuit.

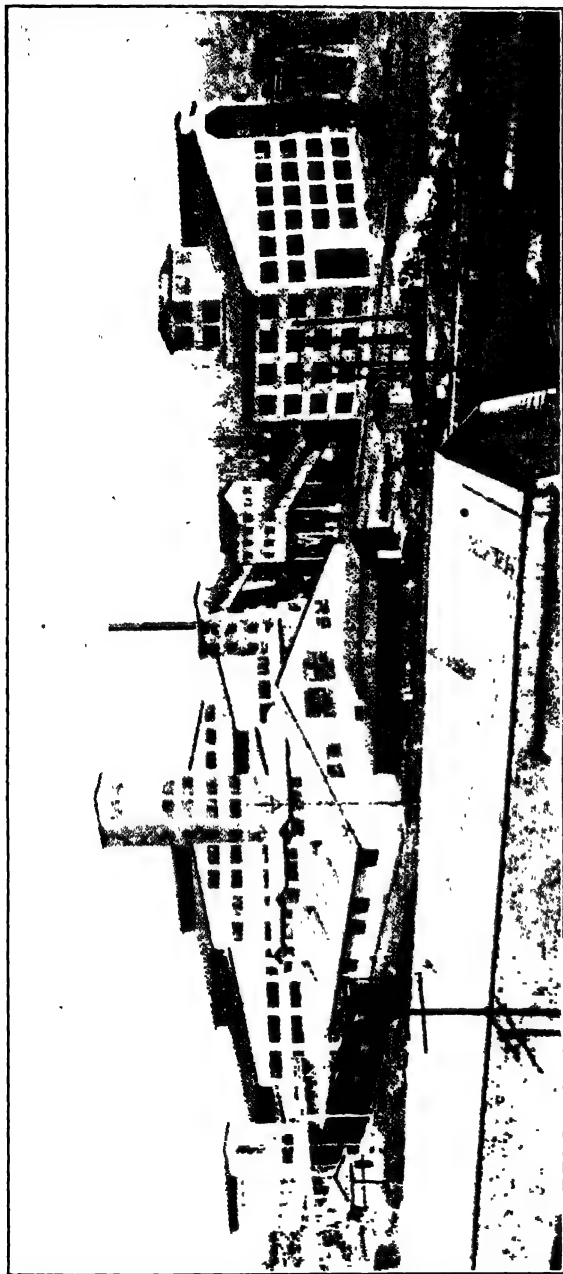


Fig. 125.—General view of Midvale plant, looking northeast. (*After Geary.*)  
Crushing plant on extreme right; sampling and grinding equipment to the right of main building; thickening in the low structure adjoining main building in the center; filter plant at extreme left over track; flotation in rear left and center.



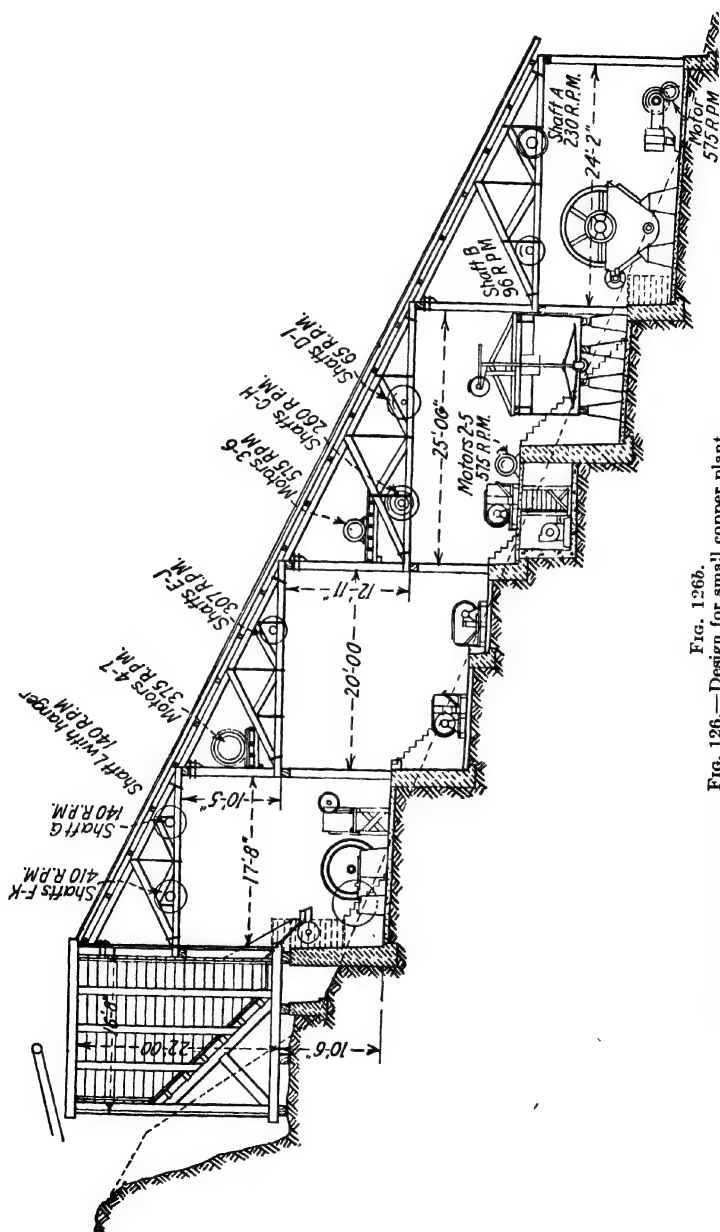


Fig. 126b.

Fig. 126.—Design for small copper plant.

Typical design for fine-grinding and flotation divisions to handle 100 tons of copper ore per day.





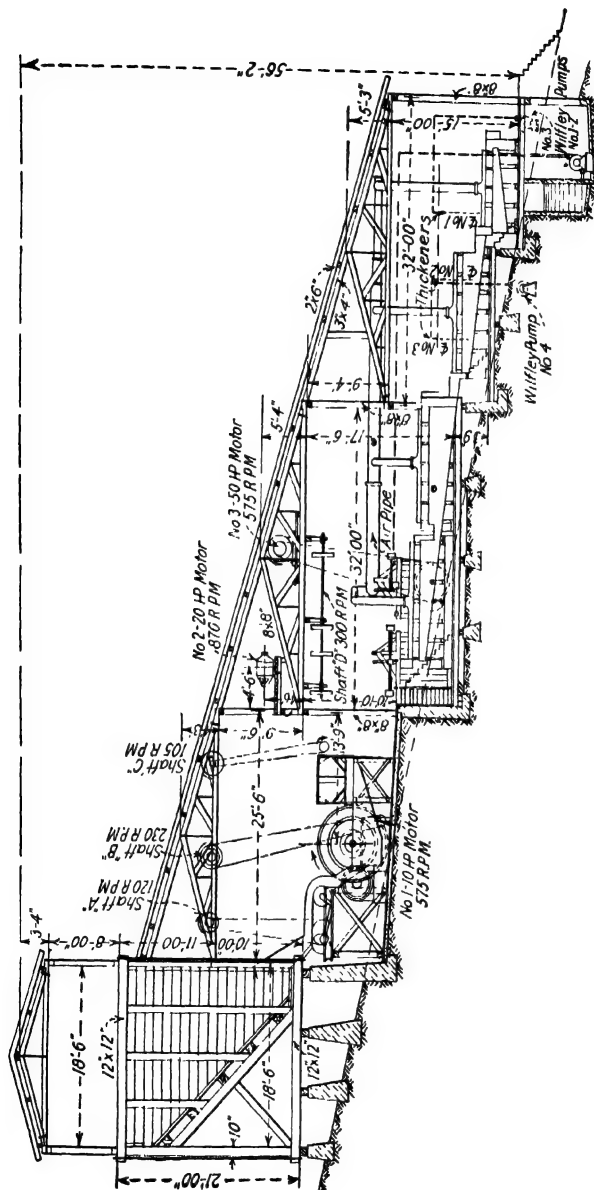


FIG. 127a and b.—Design for small lead-zinc plant.

Typical design for fine-grinding and flotation divisions to handle 100 tons of lead-zinc ore per day.

and the other in short-circuiting part of the flow from the filter well back to the thickener.

Extensive use of pumps is made to circulate pulp wherever gravity flow is not available. Elevators are still used for handling coarse material, but sand pumps have taken their place in the handling of fine pulps.

**Typical Designs.**—Figures 126 and 127 show simplified drawings<sup>(7)</sup> of the fine-grinding and flotation divisions for a typical 100-ton one-concentrate copper flotation plant and a 100-ton two-concentrate lead-zinc plant.

## CHAPTER XVI

### ELEMENTS OF COSTS

Like those of many industrial operations<sup>(27)</sup> flotation costs may be classified according to various schemes, one of which is based on the direct proportionality between the cost and some fundamental element contributing to it. Some costs are substantially *per unit of time costs*, as they are incurred regardless of the use made of the plant. Other costs are essentially *per ton costs*, as they vary with the tonnage treated. Some costs are partly dependent upon the metal content or impurity content of the ore, and to some extent are therefore *per unit of metal or per unit of impurity costs*. Finally, some costs are dependent on the profit made and may be called *per unit of profit costs*.

TABLE 151.—CLASSIFICATION OF FLOTATION COSTS

Nature of cost	Principal element contributing to the cost			
	Time	Tonnage	Metal content	Profit
I. Overhead Costs				
a. Capital (amortization)	✓			
b. Personnel (management, clerical, research, legal)	✓			
c. Insurance . . .	✓			
d. Patent royalties		✓	✓	
e. Taxes . . . . .	✓	✓		✓
II. Operating Costs				
a. Superintendence and control	✓			
b. Labor	✓	✓		
c. Power . . . . .		✓		
d. Supplies and reagents		✓	✓	

Another classification of costs is based on the time and place of expenditure. It is a two-way classification into *operating* and *overhead* costs. Operating costs represent direct expenditures made at the mill during operations. Overhead costs represent

indirect expenditures from the general office, or deriving from the initial construction of the mill, or direct expenditures for the use of a patented process. Although no hard and fast rule exists as to the broad division in which certain expenditures should be included, the summary in Table 151 meets with general approval.

Available data pertaining to costs are not stated in uniform fashion and considerable variation exists in the items that are included under each heading. Statements of total cost are therefore frequently misleading unless it is clear which items are included and which are excluded.

### OVERHEAD COSTS

**Amortization.**—Amortization costs are related to capital expenditures for plant construction. They are divisible into three classes: (a) interest on investment, (b) depreciation, and (c) obsolescence.

**Interest on Investment.**—Interest on investment is sometimes not included as a cost, as it is reasoned by some people that the return on the capital invested is the reward of the enterpriser. However, if money is borrowed for the construction of a plant, interest has to be paid on the sum borrowed before a profit can be had by the enterpriser. Interest on investment equivalent to that which should be paid to a lender appears therefore as a justifiable charge against plant operation.

In view of the risk involved in mining enterprises interest on investment in a flotation plant is at a higher rate than that prevailing for mortgages on buildings and other ordinary real estate. A rate of 1 to 3 per cent per annum higher than for real estate mortgages is adequate in most cases. For very large enterprises where risk is minimized by thorough engineering study and diversification, a rate as low as that for the best real property, or even lower, is sometimes obtained.

**Depreciation.**<sup>1</sup>—Depreciation results from the general wear and tear of plant and equipment from use, as likewise from weathering. Although some items of a plant's construction wear or disintegrate more readily than others, depreciation is frequently considered as applying equally to all parts of a plant whose useful life is therefore anticipated to terminate suddenly

<sup>1</sup> Barnes<sup>(3)</sup> considers depreciation as consisting of *natural decay*, *wear and tear*, *obsolescence*, and *inadequacy*. In this book depreciation is considered the equivalent of Barnes's natural decay, and wear and tear.

and simultaneously in all of its constituent parts. Depreciation charges are computed on the basis of an anticipated life ranging in general from 10 to 30 years.

So far as machinery is concerned, depreciation is related to repairs and replacement in a complicated manner and no standard method of cost keeping is accepted. If a plant were kept in a perfect state of repair there should be no charge for depreciation, as the annual depreciation would be made up by machinery replacements. It sometimes happens that a depreciation reserve is set up by liberal provisions, at the same time as the plant is kept in repair, thus charging twice for the same cost and hiding plant profits. Conversely depreciation provisions may be inadequate at the same time that the plant is not kept in repair, resulting in a showing of unearned profits.

**Obsolescence.**—If there were no progress in industry, and if the life of prospective plants were to equal or exceed the physical life of machinery as set by natural depreciation, there would be no necessity for considering *obsolescence*. However, that is not the case. The development and introduction of new machines or processes have caused a retirement of many machines long before the end of their physical life. In the ore-dressing field this has been the fate of many stamp mills replaced by ball mills, shaking tables replaced by flotation machines, mechanical-agitation flotation machines replaced by sub-aeration machines, deep-pulped pneumatic flotation machines replaced by shallow cells, etc.

Although obsolescence due to machinery becoming antiquated is a frequent source of unpleasant awakenings to improvident managements, the sudden scrapping of a plant because of ore shortage is perhaps even more common, particularly in the case of small properties. To illustrate, let it be assumed that a mill having a daily capacity of 100 tons is built to treat the ore from an ore body known to contain "at least" 200,000 tons of ore and "probably much more." This represents enough ore to run the mill for at least 2000 days. Amortization charges provide for depreciation in 6 years—a short time, indeed. Suppose that the ore body is "played out" after 70,000 tons—2 years' mill supply—have been treated. The enterprise finds itself at the end of 2 years with a mill physically fully two-thirds as good as it was when new, which is only one-third paid off (in the books), but for which there is no ore to treat. As it stands, the mill is worth

nothing except as scrap. Through the sale of some of the machinery the enterprise may be able to salvage a few pennies on each dollar invested, but in the main it will have to sustain a very large rather unexpected loss which really should have been charged against operations during the 2 years that the mine was worked.

In determining whether to replace obsolescent equipment by up-to-date equipment<sup>(8)</sup> most companies require the new installation to show savings sufficient to pay for itself in less than 18 to 36 months.

Interest on investment and depreciation are typical per unit of time costs, as they proceed whether or not the plant is operated. Obsolescence is a per unit of time cost as it derives from the equipment becoming obsolete. As amortization charges are a large constituent of the total treatment cost it is natural to find producers anxious to keep their plants operating all the time. Indeed, every day that the plant is not operating, and every reduction in daily tonnage handled means increased amortization charges. Conversely, crowding an increased tonnage through a given plant decreases the amortization costs.

**Magnitude of Amortization Costs.**—To illustrate the magnitude of amortization charges let it be assumed that a large plant built at a cost of \$500 per ton daily capacity is expected to last 25 years (this provision caring for obsolescence as well as depreciation) and that money at 5 per cent has been obtained for its construction. Initial amortization cost per ton is

$$\frac{500 \left[ 0.05 + \frac{1}{25} \right]}{360} = \$0.125,$$

on the basis of 360 working days per year.

The other extreme may be represented by a small plant built at the cost of \$1000 per ton, to last 5 years, on money at 8 per cent, and on the basis of 200 working days per year. Initial amortization cost is

$$\frac{1000 \left[ 0.08 + \frac{1}{5} \right]}{200} = \$1.40.$$

For a given plant interest on investment decreases from year to year, as the investment is reduced each year by the preceding year's reserve for depreciation and obsolescence. Thus the

average charge for interest on investment during the life of the plant should be one-half the charge for the *initial* year. The charge for depreciation and obsolescence, however, is constant.<sup>1</sup> In the two cases considered above, average amortization charges are \$0.090 and \$1.20, respectively.

**Overhead Personnel Costs.**—In an enterprise including concentrating in its activities a portion of the general office and management costs should be charged to concentrating. The exact amount chargeable in this way is left largely to the judgment of accountants.

That portion of research, advisory and legal work, pertaining to ore dressing in an organization using flotation is chargeable to concentration. This item is sometimes as difficult to ascertain as the concentrator's share of general office and management expenditures.

Overhead personnel costs are essentially per unit of time costs, since they proceed at pretty much the same rate regardless of business conditions.

**Insurance.**—Fire insurance for the plant and offices, and certain forms of life and accident insurance for the protection of workmen and their families, are per unit of time costs just as amortization. Fire insurance is generally a small item compared with amortization, but the aggregate of all forms of insurance constitutes a sizable sum.

**Patent Royalties.**—Formerly patent royalties were a large fraction of the total flotation cost, as much as 25 cts. per ton of ore having been charged by certain patentees. Following the expiration of the basic patents, a competitive situation has arisen among patent-exploiting companies; also patent users have appreciated how expensive litigation can be. As a result, moderate royalty rates have become established, and accepted.

Present royalties range from a fraction of 1 ct. to about 5 cts. per ton of ore treated. They are arranged on a sliding scale, charges for small plants being greater, per ton treated, than charges for large plants.

The nature of the operations may demand the use of processes or apparatus controlled by sundry patent-holding companies. In such cases several royalties may have to be paid simultaneously.

<sup>1</sup> There are other methods for determining yearly depreciation and obsolescence than the "straight-line" method (i.e., constant charge per unit time), but this method was chosen because of its wide usage<sup>(3)</sup>.

**Taxes.**—Taxes are one of the most difficult elements of cost to apportion between the various operative steps in an organization. It is impossible, for instance, to determine what burden of taxes should be carried by mining, by concentrating, by smelting, and by marketing in a complex mining and smelting corporation. In the case of a custom concentrator which pays for its ore and sells its concentrates, proper apportionment of taxes is a relatively simple problem (even if the concentrator is a unit in a large corporation dealing with the various phases of the mining industry) because the profit made by the concentrator is known.

Taxes are per unit of profit and per unit of time costs. No general rule can of course be given to indicate the extent of tax cost per ton of ore.

### CAPITAL OR FIRST COST

The capital or first cost of a flotation plant receiving coarse ore as feed ranges from \$350 to \$900 per ton of daily plant capacity (1930). The first cost of flotation plants built to treat gravity concentration tailings may be much lower as the crushing step has already been accomplished and a building to house the plant may be available.

The wide range in first cost of flotation plants is the result of many factors of which the following are the most important:

1. Number of flotation concentrates to be made.
2. Fineness of grinding required.
3. Daily tonnage.
4. Anticipated life of mill.
5. Local conditions as to accessibility and labor markets.
6. General level of commodity prices.
7. Provisions for future expansion and alteration.
8. Necessary water-supply requirements and provisions for disposal of tailing.

The effect of most of these factors on the first cost is obvious but the interrelation of some of them may not be so clear. Thus, a higher daily capacity results in a lowered cost per unit daily capacity if the same character of building and the same grade of machinery are used. But as small plants are often put up to treat small deposits or deposits of doubtful persistence, they are usually designed to have a short life and may be built of second-grade materials. Sometimes, also, small plants are equipped with second-hand machinery. Larger plants are put up only



if the ores to be treated are of proven extent; being designed for a longer life, the use of cheap buildings or equipment would be near-sighted economy. In large plants some machinery is installed in duplicate, as "spares" in order to avoid costly breakdown delays. Thus, a small mill may cost less per ton daily capacity than a large mill, if character of construction and installation outweighs tonnage.

Provision for expansion and alteration should be made in small or medium-size plants designed to treat ore bodies which are reasonably likely to expand or change with development. These provisions are an additional source of expense.

#### PRINCIPAL ITEMS IN FIRST COST

**Design and Supervision of Construction.**—Apparent cost of designing a flotation plant depends on whether the plant is designed by the staff of the operating company, by a staff of consultants, or by machinery dealers. In the first case the cost of design may become hidden among general costs of one sort or another; in the second case it is directly traceable; and in the third case it may appear as a direct charge, although it is more frequently included in the cost of the machinery.

Design and supervision of construction generally range from 3 to 10 per cent of the total first cost.

**Mill Building**<sup>(21)</sup>.—Four general types of mill buildings are commonly used: (a) wood frame with wooden sheathing, sometimes with corrugated iron; (b) steel frame covered with corrugated iron; (c) steel frame with corrugated iron walls covered inside with gunite; and (d) reinforced concrete.

Wood-frame buildings are the most primitive as well as the commonest for mills having a short life expectancy. If an abundant lumber supply is available they are also the cheapest.

Steel-frame buildings have been gaining in use in recent years for the more substantial type of structures. Corrugated-metal steel-frame buildings are inexpensive, but great temperature variations and moisture condensation should be expected within the building because of the high heat conductivity of the walls unless an insulating lining is used. Commonest insulating wall lining is gunite, a fireproof cement applied with a spraying gun. Gunite-lined buildings cost from 5 to 10 cts. more per square foot of wall area than plain corrugated-metal buildings (1923). Reinforced-concrete buildings, which are the most modern and

most expensive, are most desirable for a plant having a long life expectancy, but provisions against stresses caused by vibrating machinery should be made.

Building cost ranges from 15 to 30 per cent of the total first cost of a flotation plant.

**Machinery.**—Cost of machinery is of course the largest item in the first cost of a flotation plant. Generally speaking, it is fully one-half of the total first cost, the range being from 45 to 60 per cent of that cost.

**Erection and Installation.**—This is frequently an expensive item, particularly in connection with heavy machinery. Whereas cost of machinery is largely standard, costs of erection and installation are largely dependent on the labor market and local conditions. Erection and installation costs usually range from 10 to 20 per cent of the total cost, but they may exceed substantially the 20 per cent margin if unfavorable circumstances prevail.

#### PLANT DIVISIONS

A flotation plant consists of the following divisions: (a) crushing (including unloading and coarse-ore storage), (b) grinding (including fine-ore storage and classifying), (c) flotation, (d) concentrate disposal, (e) tailing disposal. To these divisions, which constitute the flotation plant proper, must be added auxiliary divisions for (f) water supply, (g) analytical work, (h) office work, and (i) electric-current supply.

The grinding and flotation divisions are the most expensive.

In the following pages the first cost of the flotation, concentrate disposal, and tailing disposal divisions is considered in some detail, but reference should be made to standard works and to articles published in the technical press for estimates pertaining to crushing, grinding, bin construction, water and current supply, and laboratory and office construction and equipment.

**Flotation Division.**—One-concentrate flotation requires from 3 to 7 sq. ft. of floor space per ton of ore treated daily,<sup>1</sup> and two-concentrate flotation from 7 to 10 sq. ft. Assuming an average floor height of 20 ft., the building volume required is from 60 to 140 and 140 to 200 cu. ft. per ton daily capacity, respectively. At 12½ cts. per cubic foot, the building cost should range from \$7.50 to \$17.50 and from \$17.50 to \$25.00 per ton of daily

<sup>1</sup> *E.g.*, at Cortez<sup>(11)</sup>, Nev., 585 sq. ft. were required for the flotation of 175 tons of dry silver ore per day.

capacity, respectively. Heating and lighting the building may add \$2.50 to \$10.00 per ton daily capacity.

Flotation machines (with motors if mechanically agitated) may cost from \$10 to \$75 per ton daily capacity depending upon the type of machine, complexity of circuits and ensuing capacity per cell, whether the machines are home built or shipped from the factory, and whether one or two concentrates are made. Lowest cost for flotation machines is encountered where flotation is used as a scavenging extractor, that is where the bulk of mineral to be floated is small and the mineral is readily floatable. Highest cost is encountered in selective-flotation plants where full floatability of minerals is not used, so selection will be most marked, or if minerals are so intimately locked that satisfactory liberation is not obtained without regrinding primary concentrates.

Pneumatic machines are lower in first cost than mechanically agitated or sub-aeration machines on account of the absence of moving parts, but they require blowers. This somewhat offsets their lower cost. Blowers for flotation air and piping to cells may cost from \$2 to \$10 per ton daily capacity. Cost of blowers and piping increases rapidly with decreasing size of installation, so that for very small plants the first-cost advantage of pneumatic cells reaches the vanishing point.

Cost of reagent storage, reagent tanks, reagent feeders, and piping to cells depends upon complexity of ore treatment, number of reagents, places of addition of reagents, etc. It may range from \$2 to \$16 per ton daily capacity.

Pumps for pulp circulation, elevation, and for emptying spillage sumps cost, with piping, from \$3 to \$10 per ton daily capacity for one-cycle flotation plants, and from \$6 to \$20 for two-cycle plants.

Launders, samplers, and control apparatus add \$1 to \$10 per ton daily capacity.

If a medium or large installation is contemplated a crane may be necessary (\$2 to \$10 per ton daily capacity).

Flotation division expenditures are summarized in Table 152.

At Cortez<sup>(11)</sup> (1927) cost of flotation machinery, including installation was \$6236, or \$36 per ton of daily capacity for a simple one-concentrate flotation plant. This compares with a range of \$23 to \$110, given in Table 152. At United Verde a 300-ton capacity Hunt rougher (Southwestern airlift matless cell) cost \$2000 exclusive of blower. This represents approxi-

TABLE 152.—RANGE OF FIRST COST OF FLOTATION DIVISION OF A FLOTATION PLANT (1930)

Items contributing to cost	Dollars per ton daily capacity	
	One-concentrate plants	Two-concentrate plants
1. Building		
a. Housing . . . . .	7 50 to 17.50	17.00 to 25.00
b. Heating and lighting	2.50 to 7.00	6.00 to 10.00
2. Machinery		
a. Reagent feeding . . . . .	2.00 to 10.00	7.00 to 16.00
b. Flotation machines and blowers . . . . .	15 00 to 45.00	35 00 to 75.00
c. Pumps and piping . . . . .	3.00 to 10.00	8.00 to 20.00
d. Launderers, samplers, control apparatus. . . . .	1 00 to 5.00	1.00 to 10 00
e. Crane and craneway . . . . .	0 to 6 00	0 to 10 00
f. Surge tanks . . . . .	0 to 3 00	0 to 5 00
Total, machinery only . . . . .	21 00 to 84.00	53.00 to 141.00
3. Spare flotation and pump equipment, 0 to 10 per cent.	0 to 6.00	0 to 10.00
4. Shipment, installation, and erection, 10 to 25 per cent of cost of machinery . . . . .	2 00 to 20.00	5.00 to 34.00
Grand total	33.00 to 134 50	81 00 to 220 00

mately \$7 per ton daily capacity. At the same plant<sup>(16)</sup> (1500-ton daily capacity) total cost of flotation division was \$103,700, or \$69 per ton daily capacity. Of this cost \$72,000 or \$48 per ton was for machinery, \$6700 or \$4.50 per ton for installation, and \$27,000 or \$18 per ton for housing.

In view of the fact that the lowest cost on all items is not found in one plant, nor the highest, it may be concluded that average costs for the flotation division of one-concentrate flotation plants range from \$50 to \$100 and of two-concentrate plants from \$100 to \$175 (1929). Substantial changes may occur in the future if more effective, quicker-acting reagents or more efficient aeration are introduced, as such advances in the art would naturally increase the capacity of machines and reduce correspondingly the per ton cost. The present trend to larger machines, particu-

larly noticeable in the pneumatic installations of the southwestern United States, is also a step in the direction of lowered first costs.

**Concentrate-disposal Division.**—The housing required for thickening, filtering, concentrate storage, and loading appears large in view of the small tonnage of solids handled. Twelve to forty square feet of thickener surface is required per ton of dry concentrate, depending upon the fineness and flocculability of the concentrate pulp. Thickener housing is therefore a large item of cost where it is not permissible to protect the concentrate by means of a roof only. The circular shape of thickeners necessitates a substantially larger building area (16 to 54 sq. ft. per ton of dry concentrate). At 25 ft. of building depth and a building cost of 8 cts. per cubic foot, thickener building cost is \$32 to \$108 per ton of concentrate per day.

Two to four square feet of filter-building surface per ton of concentrate represent the average building area required for filtering. With a 20-ft. ceiling and a cost of  $12\frac{1}{2}$  cts. per cubic foot, filter housing costs \$5 to \$10 per ton of concentrate per day.

If concentrate bins are installed (where it is not possible to have cars for direct loading from filter-cake conveyor belt), capacity should be sufficient to hold at least two days' production. Bin capacity should then be at least 2 tons per ton daily concentrate output and bin cost about \$10 per ton daily concentrate output.

Cost of thickeners, with motors, wiring, pumps, and piping to and from filters and from flotation division ranges from \$2 to \$4 per square foot of thickener area (1929) or \$24 to \$160 per ton of concentrate.

Filtering surface required under modern flotation conditions is much less than that required in the days of so-called "oil flotation." Average capacity is in the vicinity of 0.4 to 0.5 ton of base-metal concentrate per square foot of filtering surface. Cost of filter installations ranges from \$15 to \$45 per square foot of filter area depending upon filter capacity (1928). Filter cost is therefore \$30 to \$112 per ton of concentrate.

The first cost of the concentrate-disposal division is summarized in Table 153.

In plants having a ratio of concentration of 15:1, or even higher, as in certain copper flotation plants, the "per ton of ore" first cost of concentrate disposal is relatively small: in accordance with the above figures it ranges from \$6 to \$26. For plants making bulky concentrates, *e.g.*, many lead-zinc flotation plants,

TABLE 153.—COST OF CONCENTRATE-DISPOSAL INSTALLATIONS (1930);  
DOLLARS PER TON OF CONCENTRATE

1. Housing	
a. Thickener. . . . .	32.00 to 108.00
b. Filter . . . . .	5.00 to 10.00
c. Concentrate bin . . . . .	0 to 10.00
2. Equipment	
a. Thickeners, pumps, piping, etc. . . . .	24.00 to 160.00
b. Filters . . . . .	30.00 to 112.00
c. Concentrate belt conveyor. . . . .	0 to 10.00
<hr/>	
Total . . . . .	91.00 to 410.00

first cost of the concentrate-disposal division is considerable: the concentrate-disposal division of a plant, having a 4:1 ratio of concentration, costs from \$23 to \$102 per ton of ore treated daily.

**Tailing Disposal.**—The cost of tailing disposal is largely an operating cost, since little equipment is required. The most important first cost is that of the land on which the tailing is to be impounded. The next most important item is that of the conveyance necessary to bring the tailing from the mill to the pond. Depending upon local conditions this may be only a tailing flume, or it may involve airlifts, sand pumps, etc. As there is no standard method of tailing disposal, it is not possible to give any significant plant costs: each case has to be considered by itself.

If the tailing is thickened for water reclamation, the first cost of disposal (sometimes charged to water supply) may be high as tailing thickeners are very large and therefore expensive pieces of equipment, even without housing.

### OPERATING COSTS

Operating costs (1926–1929) for 24 mills located largely in the United States are given in Table 154. Geometric averages of costs and daily tonnage indicate an average cost of \$0.67 per ton for a 2000-ton, one-concentrate flotation plant, and of \$1.23 for a 500-ton, two-concentrate plant. The operating cost for mills treating old gravity-concentration tailings is naturally much lower as crushing costs are eliminated and grinding costs are reduced.

The data of Table 154 for one-concentrate sulfide plants are also shown in Fig. 128 which brings out clearly an inverse relation between the logarithms of the operating cost and of plant capacity. Stated analytically the relation is,

$$\log C = K \log T,$$

TABLE 154.—TOTAL OPERATING COSTS OF FLOTATION PLANTS

Plant	Location	Ore	Reference	Daily tonnage	Year	Operating cost, cents per ton
<b>One-concentrate Plants</b>						
Chief Consolidated	Eureka, Utah	Oxidized lead	(24)	125	1929	332
Cortez	... Nevada	Silver	(11)	200	1929	150
Magma	Superior, Ariz.	Copper	(20)	650	1929	74
Climax	Colorado	Molybdenum	(5)	1,000	1929	70
Westmill	Idaho	Lead	(12)	1,250	1929	79
Clarkdale	Arizona	Copper	(14)	1,500	1929	73
Cananea	Sonora, Mexico	Copper	(23)	2,400	1929	62
Phelps Dodge Corp	Arizona and Mexico	Copper	(6)	Various, 1,300 to 4,600	1928	52
Britannia	British Columbia, Can	Copper	(13)	4,000	1927	43
Hayden	Arizona	Copper	(9)	10,000	1929	40
Miami	Arizona	Copper	(17)	12,000	1927	41
Magma	Utah	Copper		30,000	1928	25
<b>Two-concentrate Plants</b>						
Black Hawk	New Mexico	Lead-zinc	(26)	160	1929	155
Utah Apex	Utah	Lead-zinc	(10)	300	1926	167
South Mill	Idaho	Lead-zinc	(12)	500	1929	158
	Spain	Lead-zinc	(7)	600	1928	90
	Northwestern U. S. A	Lead-zinc		800	1929	98
<b>Tailing Mills</b>						
	Joplin	Zinc	(2)	700	1929	21
	Tri-state District	Zinc	(13)	Not stated	1927	20
	Tri-state District	Zinc	(13)	Not stated	1927	32
	Tri-state District	Zinc	(13)	Not stated	1927	39
	Tri-state District	Zinc	(13)	Not stated	1927	28
Gem	Idaho	Lead	(28)	700	1927	25
Calumet and Hecla	Michigan	Copper (part leaching)	(4)	5,000	1929	38*

\* Excluding dredging, shore plant, and general administration costs.

in which  $C$  is the operating cost,  $T$  the daily tonnage, and  $K$  a constant (the slope of the line in Fig. 128).

Operating costs may be divided in accordance with the nature of the expenditure, that is in terms of (a) superintendence and control, (b) labor, (c) power, (d) supplies (including reagents). It may also be divided in accordance with the plant division in which it is incurred, that is into (a) crushing, (b) grinding, (c)

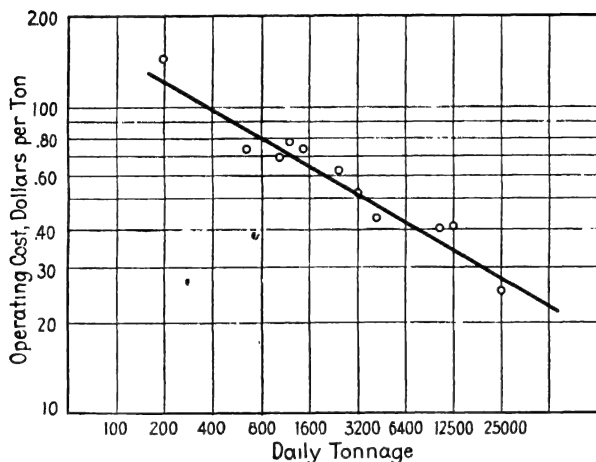


FIG. 128.—Relationship of operating costs to mill capacity.  
One-concentrate flotation plants most of which are treating copper ores (1927-30).

flotation, (d) concentrate disposal, (e) tailing disposal, (f) water supply, (g) miscellaneous (analytical work, office work, etc.). Both of these methods are used in the following pages.

**Superintendence and Control.**—Cost of superintendence and control is incurred in the form of salaries for the superintendent, assistant superintendents, metallurgists, foremen, and assayers, as well as for office upkeep and assay supplies. Except in very large mills these costs constitute a sizable portion of the total operating cost. Like most overhead costs they are per unit of time costs, and are therefore relatively magnified where tonnage is small or operations curtailed.

Relative cost of superintendence and control varies with size of mill, ranging in general from 5 to 15 per cent of the total operating cost.

**Labor.**—Labor costs constitute an important item of the total operating cost of a flotation plant. Yet flotation is strikingly



less dependent on labor problems than are other phases of the mining industry. This is because of the high degree of mechanization of flotation plants.

Variations in labor cost from plant to plant are caused by the fluctuations in unit labor cost from place to place and time to time as well as by the relative extent to which each plant is mechanized and the relative unit cost of other items, such as power.

Labor accounts for 15 to 40 per cent of the total operating costs, approximating the lower figure in a plant handling a large tonnage and the higher figure in a small plant.

To a large extent labor costs are per ton costs: more men are needed to put through a larger tonnage. It is true, of course, that if a plant is running somewhat under capacity the same number of men may be required to handle the plant, and to that extent, labor costs may be regarded as per unit of time costs. But in the main, substantial tonnage reductions or expansions bring about a reduction or expansion in the labor requirements which is definite although not proportionate.

TABLE 155.—ACTUAL LABOR REQUIREMENTS AT VARIOUS PLANTS  
(1926-1929)

Plant capacity, tons per day	Tons per man-shift	Number of flota- tion concentrates
50	7	1
125	9	1
125	10	1
175	8	2
175	11	2
200	16	1
325	13	2
450	16	2
650	24	1
1,200	28	1
1,250	27	1
1,400	20	2
1,500	28	1
2,400	16*	1
3,000	26	1
4,600	33	1
5,000	24	2
10,000	35	1
12,500	31	1
25,000	62	1

\* Partly uses inferior low-cost labor.

Skilled operators are required for successful operation. A high cost per unit of labor is therefore the rule. But since one man may handle a very large tonnage, the total labor cost per ton handled is low in comparison with that in other metallurgical operations. In countries where unskilled labor at low cost is the rule, trained imported operators may be necessary in conjunction with unskilled native laborers. In those cases the number of tons milled per man-shift is reduced, but the total cost may not be any higher.

Table 155 gives labor requirements at various plants employing a good grade of labor, and operating at or near capacity (1929).

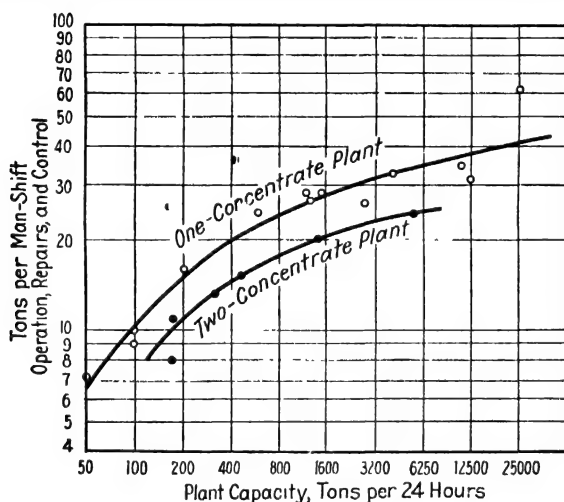


FIG. 129.—Total labor requirements of flotation plants.

From Fig. 129 it is apparent that 4 to 6 tons is the average difference in output per man-shift between one- and two-concentrate plants.

Since large plants afford more permanent employment their unit labor cost (man-shift) is somewhat smaller.

In flotation plants a large portion of the labor employed is engaged in operation of apparently secondary importance, such as attending ore bins, loading concentrates, disposing of tailings, or as watchmen. Repair gangs also constitute an important item in labor cost. This is shown by Table 156, in which are presented the labor expenditures of three typical copper flotation plants for 1929. It is seen that the total labor represented by mill operators, that is attendants to crushing, grinding, flotation, thickening, and filtering machinery, is from one-quarter to one-half of the total.

TABLE 156.—LABOR COST AT SEVERAL ARIZONA COPPER FLOTATION PLANTS, CENTS PER TON TREATED

Operating divisions	Nevada Consolidated plant, Hayden <sup>(9)</sup> , 10,000 tons per day		United Verde plant <sup>(14)</sup> , 1,500 tons per day		Magma plant <sup>(20)</sup> , 650 tons per day	
	Operating	Repairs	Operating	Repairs	Operating	Repairs
Crushing.....	2.10	1.40	*	*	2.29	1.19
Grinding. . .	0.81	0.66	3.27	1.19	1.60	4.78
Flotation . .	1.50	0.34	2.16	0.43	2.88	1.22
Concentrate disposal .....	0.44	0.25	2.11	0.44	...	0.20
Total, crushing, grinding, flotation, and concentrate disposal, operation only....	4.85		6.54		6.77	
Tailing disposal	0.12	0.72	0.36	0.07	1.00	0.26
Water supply ..	0.25	0.12	....	0.10		0.48
Assaying and testing.....	0.76	0.14	3.07	0.02	3.00	0.46
Miscellaneous ..	0.91				3.70	0.91
Grand total...	6.89	3.63	10.97	2.25	14.47	9.42
	10.52		13.22*		23.89	

\* Excluding crushing.

At a typical installation, milling 325 tons daily of a complex lead-zinc-iron ore and making two concentrates, the labor crew was as follows:

Crushing . . . . .	2 men for 2 shifts =	4	man-shifts.
Grinding.. . . .	1 man for 3 shifts =	3	man-shifts.
Flotation. . . . .	1 man for 3 shifts =	3	man-shifts.
Filtering . . . . .	1 man for 3 shifts =	3	man-shifts.
Concentrate loading. . . . .	2 men for 1 shift =	2	man-shifts.
Tailing disposal. . . . .	3 men for 1 shift =	3	man-shifts.
Repair crew, average...		2.5	man-shifts.
Electrician, average . . . . .		0.25	man-shift.
Assaying.....	3 men for 1 shift =	3	man-shifts.
Total .....		23.75	man-shifts.

In this instance the flotation operator acted as shift boss, and no additional "shifter" was required.

At a very large plant (handling 20,000 to 30,000 tons per day) there are 400 men on the pay roll, but only 32 men per shift are employed in the fine-crushing and grinding divisions, and five men per shift in the flotation division. In other words, in the flotation division one man handles up to 2000 tons of ore per shift.

At a small plant, treating 175 tons daily of lead ore, one man per shift is required for grinding and flotation, one man for one shift for crushing, and one man for one shift for assaying.

**Power.**—Total power (or rather energy) costs are determined essentially by (a) tonnage treated, (b) character of ore, and (c) cost of unit power.

For a given ore, power consumption is proportional to the tonnage handled. For dissimilar ores treated in plants of similar size different amounts may be required per ton of ore, yet the range in power consumption with different ores is not as large, for instance, as the range in labor requirements (tons per man-shift) for mills of various sizes. Power consumption is substantially independent of plant capacity.

Cost of unit power varies greatly. It depends primarily upon local conditions, size of plant, and whether power is purchased or made at the concentrator. Due to the relatively constant

TABLE 157.—POWER CONSUMPTION AT FLOTATION PLANTS (1927-1930)

Plant	Daily tonnage	Power, kilowatt-hours per ton	Type of ore
Magma Copper Company <sup>(20)</sup>	650	18 9	Sulfide copper
United Verde <sup>(14)</sup>	1,500	18 5	Sulfide copper
Phelps Dodge concentrators <sup>(6)</sup>	1,500	14 45	Sulfide copper
	3,000		
	4,000		
	4,600		
Morenci branch, Phelps Dodge <sup>(19)</sup>	4,000	14 0	Sulfide copper
Britannia <sup>(15)</sup> . . . . .	4,000	14 1	Sulfide copper
Hayden, Nevada Consol. <sup>(9)</sup>	10,000	11 1	Sulfide copper
Inspiration <sup>(18)</sup> . . . . .	20,000	13 9	Sulfide copper
San Francisco Mines of Mexico <sup>(1)</sup>	1,000	27.9	Sulfide lead-zinc
Chief Consolidated <sup>(24)</sup> . . . . .	125	51.2	Oxidized lead

character of the power load, flotation plants are deemed desirable customers by public utilities and can therefore buy power at a lower rate than many industrial concerns whose power load is more variable.

In North America power costs from 0.2 to 3.0 cts. per kilowatt-hour, averaging about 1.0 ct.

Table 157 shows total power consumption at various plants.

Power requirements for one-concentrate plants range from 12 to 20 kilowatt-hours per ton depending on the fineness to which the ore is ground. Two-concentrate plants involve practically double the flotation and concentrate-disposal power consumption of one-concentrate plants. Also, they are likely to be applied to finer textured ores and on a smaller tonnage. Data are scant, but an estimate of from 20 to 40 kilowatt-hours per ton is not out of reason.

Relative power costs in the various divisions of flotation-plant operation are indicated by Table 158. • Approximately three-fifths of the total power is expended in crushing and grinding.

TABLE 158.—PERCENTAGE POWER COSTS OF VARIOUS DIVISIONS  
IN SEVERAL FLOTATION PLANTS  
(Mill division)

Plant	Crushing, screening, and conveying	Grind- ing and classi- fying	Flota- tion	Concen- trate disposal	Water supply	Mis- cella- neous
United Verde	18*	52	21	5	1	3
Magma	18	34	35	....	8	5
Hayden	33	34	16	2	14	1
Morenci	21	51	19	4		5
Inspiration	4	65	20	3	5	3
San Francisco	4	38	46	3	1	8
Chief Consolidated	4	41	42	10		3
Average	14.6	45 0	28 4	3 9	4 1	4 0

\* Partly estimated

As the trend is to finer grinding, it is likely that the relative power cost for crushing and grinding will increase further in the future (Table 159).

Of the power expenditure in the flotation division, the bulk is taken up by operation of flotation machines or of blowers (if pneumatic machines are used).

TABLE 159.—POWER CONSUMPTION AND DISTRIBUTION—PHELPS  
DODGE CONCENTRATORS  
(After Cramer<sup>(6)</sup>)

Year	Kilowatt-hours per dry ton				Percentage of total power used by		
	Total	Crushing and grinding	Flotation	Miscellaneous	Crushing and grinding	Flotation	Miscellaneous
1924	15 21	9.76	3.35	2.10	64.17	22.02	13.81
1925	14 75	9.74	2.87	2 14	66.03	19.46	14.51
1926	14 14	9.78	2.00	2 36	69.17	14 14	16.69
1927	14 49	10 94	0.91	2.64	75.50	6 28	18.22
1928 (5 mo.)	14 45	10 89	0 91	2 65	75.36	6.30	18.34

**Supplies.**—Supply costs are strictly per ton, and therefore a nearly constant expenditure per ton treated regardless of tonnage handled. The percentage operating expenditure represented by supplies is the largest item in a flotation plant. It varies from one-fifth to one-half of the total cost.

Figure 130 shows schematically the relationship between total operating cost and relative operating costs of each type for typical plants of various rated capacities. It should be understood that the figures given are of a very general nature.

The supplies most extensively used are water, steam, flotation reagents, balls, rods, and liners. Spare parts for fast-wearing equipment such as screen cloth or punched-screen sheets, pump runners and casings, flotation-machine impellers, flotation canvas, pipe, roll shells, elevator buckets, assay and office supplies are also of importance.

With the exception of water, some reagents, steel balls, and steam, the supplies are purchased from the makers or jobbers at wholesale or semiretail prices. As a result, the price per unit shows little variation between large and small user.

Large plants find that it pays to make balls from scrap rather than to buy them and pay freight<sup>(22)</sup>. In that case a cheap low-grade ball is at an advantage over an expensive high-grade ball; the converse is true in the case of many small mills.

Steam is supplied locally at costs that vary widely in accordance with the cost of fuel and whether the steam is a by-product or the object of a special installation.

The cost of water ranges greatly, depending upon the extent of the works needed to bring the supply to the mill and whether it has to be reclaimed or not.

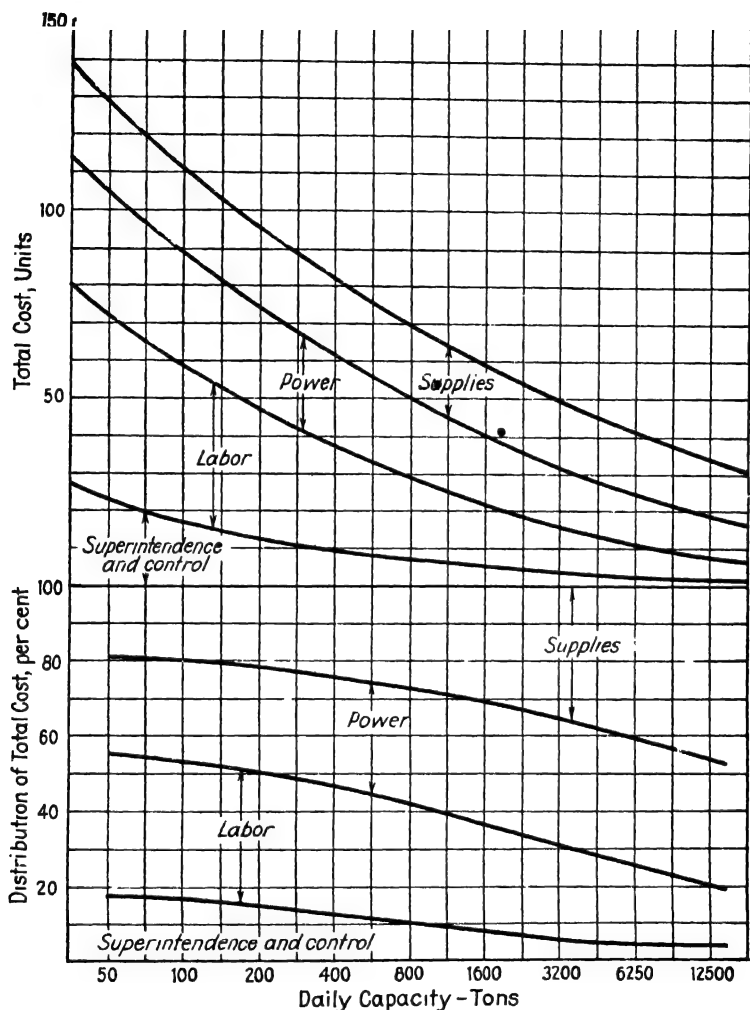


FIG. 130.—Contributions of various items to total operating cost.

Lime, and in some instances xanthates, have been manufactured by the user at or near the flotation plant. In the case of xanthates it is doubtful whether it pays for the flotation plant to manufacture its own supply, as the quantity is small even for a very large plant, and freight on water and all waste products of

the xanthate-generating reaction have to be paid if the reagent is manufactured at the mill. Furthermore, an unusual skill is required to make the reagent: if the operator's time and the grade of product are figured in the cost of making the reagent at the plant, this cost is, in most cases, higher than the purchase cost of a standard brand. Lime, on the other hand, is used in such large amount, and limestone is so generally available, that it pays to manufacture it locally.

Data on reagent consumption have been given in Chap. V and also in Chaps. VIII to XIII.

To some extent, reagent cost is a per unit of metal or per unit of impurity cost, as more of certain reagents is needed if the metal or impurity content of the ore is increased. This relationship although definitely observable is so overshadowed by other variables that it may well be passed over lightly.

TABLE 160.—PHELPS DODGE CONCENTRATORS—CONCENTRATING COSTS  
(After Cramer.)

Mill division	1923	1924	1925	1926	1927	1928, 5 months
Crushing	\$0 089	\$0 079	\$0.082	\$0.081	\$0 083	\$0 084
Grinding	0 250	0 220	0 204	0 188	0 200	0 189
Flotation	0 260	0 217	0 150	0 133	0 095	0 088
Concentrate handling	0 035	0 029	0 025	0 021	0 020	0 019
Tailing disposal.	0 034	0 047	0 028	0 018	0 022	0 021
Water	0 080	0 076	0 079	0 069	0 063	0 060
Miscellaneous direct	0 116	0 087	0 090	0 074	0 077	0 067
Direct cost	\$0 864	\$0 755	\$0.658	\$0.584	\$0.560	\$0 528

TABLE 161.—PHELPS DODGE CONCENTRATORS—RELATIVE CONCENTRATING COSTS, PER CENT  
(After Cramer.)

Mill division	1923	1924	1925	1926	1927	1928
Crushing	10 3	10 5	12 4	13 9	14 8	15 9
Grinding	28 9	29 2	30 9	32 2	35 7	35 9
Flotation	30 2	28 7	22 8	22 7	17 0	16 5
Concentrate disposal	4 0	3 8	3 8	3 6	3 6	3 6
Tailing disposal	3 9	6 2	4 3	3 1	3 9	4 0
Water	9 3	10 1	12 0	11 8	11 3	11 4
Miscellaneous	13 4	11 5	13 8	12 7	13 7	12 7



**Relative Costs of Various Divisions.**—Of the various plant divisions contributing to the cost of a flotation plant, the crushing, grinding, and flotation divisions account for the bulk of the expense. The relative cost of the flotation division proper is gradually decreasing as may be seen from Tables 160 and 161<sup>(6)</sup>. Average relative costs for the various divisions of 10 representative plants are presented in Table 162.

TABLE 162.—AVERAGE RELATIVE PLANT-DIVISION COSTS FOR TEN REPRESENTATIVE PLANTS (1929)

Mill division	Cents per ton	Per cent
Crushing, screening, conveying, storing . .	14 2	20 3
Grinding and classifying	20 0	28 7
Flotation . .	25 5	36 4
Concentrate disposal . . . . .	2 5	3 6
Tailing disposal. . . . .	2 1	3 0
Water supply . . . . .	2 1	3 0
Miscellaneous . . . . .	3 5	5 0
Total . . . . .	69 9	100 0

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## CHAPTER XVII

### CHOICE OF ORE-TREATMENT METHOD

Choice of flotation for ore treatment should be justifiable on economic grounds. Construction of a flotation plant to treat an ore should not be undertaken before it is evident by test that more money cannot be made by adopting some other treatment. Shipping the ore directly to the consumer or smelter, leaching, or gravity concentration may be indicated by analysis as more advantageous than flotation.

In the operation of a flotation plant the expediency of making a collective concentrate may be indicated for certain ranges in metal prices. Conversely, the making of several concentrates is advantageous for other ranges in metal prices. Also, the advisability of bending one's efforts to making a higher grade concentrate or a higher recovery is a function of the metal market. In most cases pertaining to metal mining the presence of several valuable metals in each concentrate makes the problem of most remunerative operation one of great complexity, and one for which an approximate solution only may be hoped.

Problems dealing with the choice of an ore-treatment method hinge on a proper appreciation of the demands of the consumer for the product of the flotation plant (*i.e.*, of the smelter in the case of metal products). The value of a concentrate to a smelter, in turn, depends upon the market for metals, grade of the concentrate, impurity content of same, and upon the general nature of the other ores and concentrates received by the smelter. Smelters pay for concentrates according to schedules embodied in contracts for ore purchases.

### SMELTER SCHEDULES

Smelter schedules for copper, lead, and zinc concentrates are rather well standardized. They are typified by the simplified examples on the following pages (Tables 163'to 165).

**Copper-smelting Schedules.**—Sulfur, silica, alumina, and iron are the chief bulky impurities in copper flotation concentrates.

Their elimination from the concentrate is the object of the smelting operation, yet penalties are not imposed on sulfur or iron whose presence is desirable for the production of matte—the

TABLE 163.—TYPICAL COPPER-SMELTER SCHEDULE  
(Southwestern United States)

**Payments:**

*Gold*.—If 1 oz. or more (total), pay for all the gold at \$19.00 per oz.

*Silver*.—If 1 oz. or more (per ton), pay for 95 per cent of the metal at New York quotation.

*Copper*.—If 3 per cent or more, pay for 90 per cent of dry assay (wet assay less one unit\*) at New York quotation for electrolytic copper less 3 cts. per pound.

*Iron*.—Pay at 5 cts. per unit.\*

*Lime*.—If over 3 per cent, pay for all at 6 cts. per unit.\*

**Charges:**

*Insoluble*.—Charge at 10 cts. per unit.\*

*Arsenic, Antimony, and Bismuth*.—Three per cent free, excess charge at 50 cts. per unit.\*

*Treatment charge* on 3 per cent copper, \$3.00 base. Reduce charge by 10 cts. for each unit\* of copper in excess of 3 per cent (dry).

\* One unit = one per cent, or 20 lb. per ton

TABLE 164.—TYPICAL LEAD-SMELTER SCHEDULE  
(Rocky Mountain)

**Payments:**

*Gold*.—If over 0.02 oz. per ton, pay for all the gold at \$19.00 per ounce.

*Silver*.—If over 1.0 oz. per ton pay for 95 per cent of the silver content at the New York quotation (minimum deduction 0.5 oz. per ton).

*Lead*.—If over 3 per cent, pay for 90 per cent of the lead content, determined on the basis of the wet assay of the fire button, at the New York quotation less 1.65 cts. per pound.

*Copper*.—Pay for 80 per cent of the copper content (minimum deduction, one unit\*), on the basis of the wet assay at the New York quotation for electrolytic copper, less 6 cts. per pound.

*Iron*.—Pay at 6 cts. per unit.\*

**Charges:**

*Insoluble*.—Charge at 10 cts. per unit.\*

*Zinc*.—Six per cent free; excess over 6 per cent at 30 cts. per unit.\*

*Sulfur*.—Two per cent free; excess over 2 per cent at 25 cts. per unit;\* maximum charge \$2.50 per ton.

*Treatment Charge*.—\$2.50 per ton on the basis of 30 per cent lead content. Increase charge by 10 cts. for each unit\* of lead under 30 per cent, and decrease it by 10 cts. for each unit\* in excess of 30 per cent.

\* One unit = one per cent, or 20 lb per ton

TABLE 165.—TYPICAL HYDROELECTROLYTIC ZINC-REFINERY SCHEDULE  
(Rocky Mountain)**Payments:**

*Zinc*.—If less than 45 per cent Zn, pay for 77 per cent of the zinc at St. Louis market; if 45 per cent Zn, or over, pay for 80 per cent of the zinc.

*Lead*.—Pay for 80 per cent of excess over 4 per cent at New York price less 2 cts. per pound.

*Silver*.—If over 1.0 oz. per ton, pay for 80 per cent of the total silver at New York price.

*Gold*.—If over 0.01 oz. per ton pay for 80 per cent at \$20.00 per ounce.

**Charges:**

*Treatment Charge*.—Base \$18.00 per dry ton when zinc is 4.0 cts. per pound, or less, if less than 45 per cent zinc. Add to charge \$2.50 for each 1 ct. rise in price of zinc over 4 cts. per pound. If 45 per cent zinc or more, add to charge \$2.75 for each 1 ct. rise in price of zinc over 4 cts. per pound. 6 per cent insoluble free; if over 6 per cent add 25 cts. per unit\* in excess; if under 6 per cent deduct 25 cts. per unit\* in deficiency.

\* One unit = one per cent or 20 lb per ton.

first step in copper smelting. But penalties are imposed on the so-called "insoluble" which is a crude measure of the silica and alumina content. In the case of smelters needing more iron than they receive from current shippers a bonus for iron may be paid. Generally, however, iron is available in excess (as pyrite). A charge for briquetting concentrate is made by some smelters, but the tendency is to discontinue this charge, since the blast furnace has become obsolete. Payment for precious metals and copper is made at current market price (or at the quotation for some predetermined date) less certain deductions covering the costs of refining the copper, shipping the bullion, and marketing the products, as well as the profit of the smelter.

Calculation of the smelter returns from a smelter schedule is typified by the following example:

**Problem 1.**—A carload of copper flotation concentrate containing gold, 0.15 oz. per ton; silver, 7.3 oz. per ton; copper, 27.7 per cent (wet assay); insoluble, 12 per cent; iron, 28 per cent; and lime, 2 per cent, is shipped to a smelter of the southwestern United States. What payment is made to concentrator per ton of concentrate and per pound of copper (crediting minor metals)? Silver at 50 cts. per ounce, copper at 13 cts. per pound. No freight charge.

## Solution.

		Dollars per Ton of Concentrate	
		Credit	Debit
Gold:	$0.15 \times 19.00$ .....	2.85	
Silver:	$0.95 \times 7.3 \times 0.50$ .....	3.47	
Copper:	$0.90 \times (27.7 - 1.0) \times 20$ $\times (0.13 - 0.03)$ ..	48.06	
Iron:	$28 \times 0.05$ .....	1.40	
Lime:			
Insoluble:	$12 \times 0.10$ .....		1.20
Treatment:	$3.00 - (26.7 - 3.0) (0.10)$ ..		0.63
		55.78	1.83
		1.83	

Net smelter payment, per ton of dry concentrate . . . 53.95

Net payment, per pound of copper,  $\frac{53.95}{554} = \$0.0974 = 9.74$  cts.

Table 166 illustrates, according to a California schedule<sup>(4)</sup>, the payment per pound of copper in flotation concentrates containing various amounts of copper.

TABLE 166.—NET PRICE PER POUND OF COPPER PAID BY SMELTER FOR FLOTATION CONCENTRATE (California Schedule)

Copper in concentrate, per cent	Payment, cents per pound of copper, if refined copper is worth:					
	8 cts.	10 cts.	12 cts.	14 cts.	16 cts.	18 cts.
5	0	0	0 92	2 40	3 88	5.36
10	0 98	2.72	4.46	6 20	7 94	9.68
15	1 99	3.81	5 64	7 47	9.29	11.12
20	2 49	4 38	6 23	8 10	9.97	11.84
25	2 79	4 69	6 58	8.48	10 38	12 27
30	2 98	4 91	6 82	8 73	10.65	12.56
35	3 14	5 06	6 99	8 91	10.84	12.77
40	3 25	5.18	7.12	9.05	10.99	12.92

Table 166 shows, for instance, the marked dependence of payment on the market price for the metal. It shows also the great increase in payment per pound of copper for a small increase

in grade in low-grade material, but the small increase in payment per pound of copper for a corresponding increase in grade in high-grade material. Thus the average appreciation represented by the production of a 20 per cent concentrate instead of a 15 per cent concentrate is 9.6 per cent of the per-pound-of-copper value of the lower grade concentrate, but the average appreciation represented by the production of a 40 per cent concentrate instead of a 35 per cent concentrate is only 1.6 per cent of the per-pound-of-copper value of the lower grade concentrate. If a higher grade concentrate were to be obtained at the expense of recovery, the decrease in recovery could be as high as 9.6 per cent of the net recovery in the first instance, but not over 1.6 per cent in the second instance.

Likewise, it may be observed from Table 166 that an increase in the grade of concentrate is of greater proportionate benefit in days of low metal prices. This is another instance of the desirability of *operating a concentrator for recovery in boom days and for grade in times of depression.*

**Lead-smelting Schedules.**—The commonest bulky impurities in lead concentrates are sulfur, silica, alumina, iron, and zinc. All of these except iron are undesirable and have therefore to be penalized: sulfur necessitates special roasting operations; silica and alumina have to be fluxed in slag; and zinc makes a pasty slag and reduces the capacity of the furnace—hence increases the smelting cost. Iron together with lime is needed to flux the silica of siliceous lead ores which are generally mixed with flotation concentrates for smelting. The increasing production of flotation concentrates and the decreasing availability of siliceous oxidized ores (which are being concentrated to an increasing extent) makes iron less desirable for silica fluxing than it used to be. It is likely that in some districts a silica bonus and iron penalty will become established if the present tendency in concentrate production continues to manifest itself.

Arsenic, antimony, and bismuth are impurities of small bulk but great inconvenience in smelting and refining. They are penalized heavily. As considerable variation in the penalties exists<sup>(5)(4)</sup>, and as arsenic, antimony, and bismuth are fortunately uncommon in lead concentrates, no provision for them is entered in the simplified schedule presented in Table 164.

Calculation of the smelter returns from a lead concentrate is typified by the following example:

**Problem 2.**—A lead flotation concentrate containing gold, 0.04 oz. per ton; silver, 2.5 oz. per ton; lead, 51.5 per cent; copper, 2.3 per cent; iron, 10 per cent; zinc, 7 per cent; sulfur, 21.7 per cent; and insoluble, 6 per cent, is shipped to a lead smelter. What payment is made to concentrator per ton of concentrate if freight amounts to \$2.25 per ton of wet concentrate containing 10 per cent moisture? Crediting minor metals to lead, what is the payment per pound of lead? Lead at 6 cts. per pound, copper at 14 cts. per pound, silver at 50 cts. per ounce. Wet assay on fire button indicates a lead content 1.5 per cent lower than chemical analysis.

**Solution.**

		Dollars per Ton of Concentrate	
		Credit	Debit
Gold:	$19.00 \times 0.04$ .....	0.76	
Silver:	$(2.5 - 0.5) (0.50)$ .....	1.00	
Lead:	$0.90 \times (51.5 - 1.5) \times 20 \times (0.06 - 0.0165)$	39.15	
Copper:	$(2.3 - 1.0) \times 20 \times (0.14 - 0.06)$	2.08	
Iron:	$10 \times 0.06$ .....	0.60	
Insoluble:	$6 \times 0.10$ .....		0.60
Zinc:	$(7.0 - 6.0) (0.30)$ .....		0.30
Sulfur:	Maximum.....		2.50
Treatment:	$2.50 - (51.5 - 1.5 - 30.0) (0.10)$ ..		0.50
		43.59	3.90
		3.90	
Net smelter payment		39.69	
Freight	$\frac{2.25}{0.90}$	2.50	

Net concentrator receipt per ton of dry concentrate. . . \$37.19

Payment, per pound of lead =  $\frac{37.19}{1030} = \$0.0361 = 3.61$  cts.

Table 167 illustrates the payment per pound of lead in flotation concentrates containing various amounts of lead according to the Bunker Hill schedule<sup>(5)</sup>. In this instance, as well as in that of the payments for copper in a copper concentrate, the relative appreciation per unit increment in metal content in the concentrate decreases rapidly with grade of concentrate as well as with increased price for the refined metal. Thus the average relative appreciation in substituting a 50 per cent concentrate for a 40 per cent concentrate is 9.2 per cent of the per-pound-of-metal



TABLE 167.—NET PRICE PER POUND OF LEAD PAID BY SMELTER FOR LEAD FLOTATION CONCENTRATE\*  
(After Bunker Hill open schedule<sup>(5)</sup>.)

Lead in concentrate, per cent	Payment, cents per pound of lead in concentrate, if refined lead is worth at New York:					
	4 cts.	5 cts.	6 cts.	7 cts.	8 cts.	9 cts.
20	0.09	0.93	1.77	2.62	3.46	4.31
30	0.89	1.75	2.61	3.48	4.34	5.20
40	1.29	2.16	3.03	3.91	4.78	5.65
50	1.53	2.41	3.28	4.16	5.04	5.92
60	1.69	2.57	3.45	4.33	5.22	6.10
70	1.80	2.68	3.57	4.45	5.34	6.22
80	1.80	2.77	3.66	4.55	5.44	6.32

\* Assuming no penalties for impurities or bonuses for minor metals.

value of the lower grade concentrate, but the relative appreciation in substituting an 80 per cent concentrate for a 70 per cent concentrate is only 2.8 per cent of the per-pound-of-metal value of the lower grade concentrate. Also, the relative appreciation in substituting a 50 per cent concentrate for a 40 per cent concentrate is 18.3 per cent if refined lead is worth 4 cts.; 8.3 per cent if it is worth 6 cts.; 4.8 per cent if it is worth 8 cts. This again shows the desirability of making a high-grade concentrate if the price of the metal is low, and a high recovery if it is high.

**Zinc Schedules.**—Two general types of zinc-concentrate schedules are in force, depending upon the treatment applied to the concentrate (hydroelectrolytic or retort).

In the hydroelectrolytic refining of zinc concentrates, which is the principal refining method for flotation concentrates, the main bulky impurities are sulfur and iron. Ores or concentrates are not penalized directly for sulfur and iron. But the treatment charge is large enough to take care of the cost of eliminating them. Various impurities occurring in minor quantity (*e.g.*, cobalt, germanium, etc.) are highly objectionable, but no standard provision is made in the schedules to take care of them.

Table 168 illustrates the payment per pound of zinc in flotation concentrates containing various amounts of zinc according to the Anaconda open schedule. The figures show that there is relatively more advantage in securing a high-grade product in a zinc concentrate than in a lead concentrate or in a copper con-

TABLE 168.—NET PRICE PER POUND OF ZINC PAID BY HYDROELECTROLYTIC ZINC REFINERY FOR FLOTATION ZINC CONCENTRATE\*  
(According to Anaconda open schedule.)

Zinc in concentrate, per cent	Payment, cents per pound of zinc, if price of the refined metal is, per pound:				
	4 cts.	5 cts.	6 cts.	7 cts.	8 cts.
35	0.51	0 92	1.33	1.75	2.16
40	0.83	1.29	1 74	2.20	2.66
45	1 20	1 69	2 19	2 57	3.18
50	1 40	1 92	2 45	2 97	3.50
55	1 56	2 11	2 66	3 21	3.76
60	1.70	2 27	2 84	3 41	3 98
65	1.82	2.40	2 99	3.58	4.17

\* Assuming no penalizable impurity.

centrate, as the payment per pound of zinc varies more with grade of concentrate than does the payment for lead or copper. This is shown also by Fig. 131. For a mill located at some distance from the refinery, the making of a high-grade concentrate, even at the expense of recovery, is of still greater advantage. This is shown by a comparison of Tables 169 and 168. Table 169 shows the net value of the zinc concentrate per pound of zinc *at the concentrator*, for a shipper having

TABLE 169.—NET VALUE OF ZINC, PER POUND, AT CONCENTRATOR, IF IN THE FORM OF CONCENTRATES OF VARIOUS GRADES, FOR VARIOUS LEVELS OF THE ZINC MARKET

(Freight on concentrate is \$4 per ton if the concentrate is worth \$20 per ton, or less; \$5 if worth up to \$35; and \$6 if worth over \$35.)

Zinc in concentrate, per cent	Value, cents per pound of zinc if price of the refined metal is, per pound:				
	4 cts.	5 cts.	6 cts.	7 cts.	8 cts.
35	0	0 35	0 76	1 19	1 59
40	0 33	0 79	1 24	1 70	2.04
45	0.75	1 25	1 74	2.13	2.63
50	1 00	1 52	1 95	2 47	2 90
55	1 20	1 66	2 21	2 67	3.22
60	1 28	1 85	2 42	2 91	3.48
65	1 43	2.02	2.53	3.12	3.71

to pay a freight charge of \$4.00 per ton for shipments valued at the refinery at \$20.00 per ton or under, \$5.00 for shipments valued up to \$35.00, and \$6.00 for shipments valued higher than \$35.00.

Figure 131 summarizes the relationship between grade of concentrate, market price, and payment by smelter as compared with gross (refined-metal) value of base-metal concentrates. The margin between apparent and true value appears large indeed.

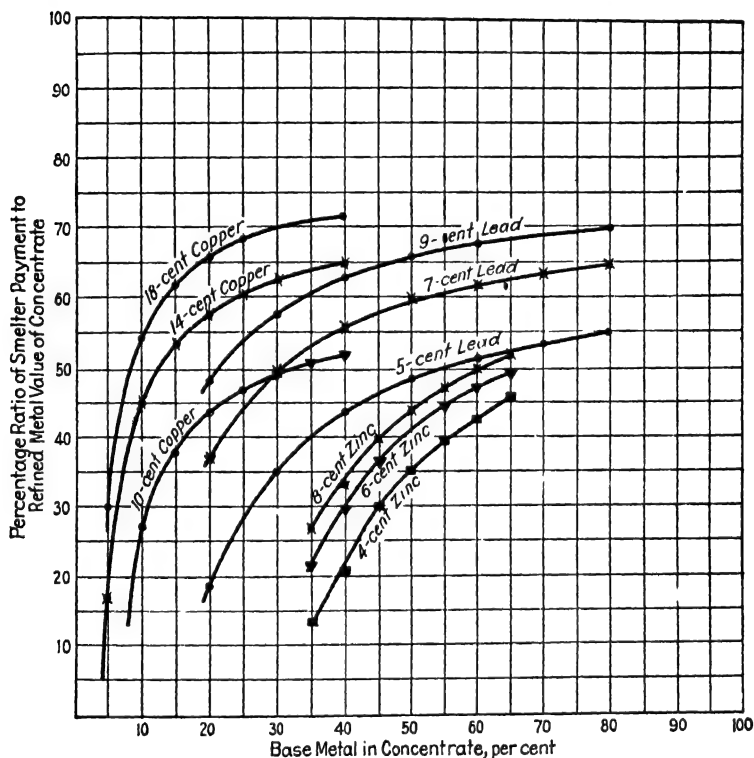


FIG. 131.—Relation of smelter payment to apparent gross value of concentrate and to grade of concentrate.

This reflects the cost of the many steps from concentrate to finished product, and more particularly of smelting, transportation, refining and marketing of metal, as well as smelting and refining losses. The percentage of the gross value of the metals which is received by the shipper is least for the least valuable of the three base metals, zinc, and greatest for the most valuable, copper.

# CHOICE BETWEEN FLOATING BEFORE SMELTING AND DIRECT SMELTING

The principal factors that enter in this general problem are the following:

- a. Grade of feed.
- b. Possible grade of concentrate or concentrates and corresponding recovery.
- c. Shipping costs on feed and concentrate.
- d. Cost of concentrating.

**Effect of Grade of Feed.**—Although recoveries by flotation are generally higher as the feed is higher—for a given grade of concentrate—the net amount of metal lost per ton concentrated is greater on high-grade ores. Also, on high-grade ores the relative appreciation in returns deriving from flotation before smelting is less than the corresponding appreciation in returns on low-grade ores. Upon consideration of successively richer ores the point is therefore approached or reached where no profit is derived by flotation before smelting instead of smelting directly. This is illustrated by the following idealized problems.

**Problem 3.**—A series of similar ores from a small mine contain 3, 5, 8, 10, and 12 per cent copper. Flotation tests show that it is possible in every case to make a 25 per cent concentrate, corresponding tailings containing 0.3, 0.4, 0.5, 0.6, and 0.7 per cent copper. Haul to smelter costs \$2.00 per dry ton for ore, and \$5.00 per dry ton for concentrate. Dressing cost, including overhead, would be \$2.50 per ton of ore. What is the increment in returns, expressed in cents per pound of copper in the ore, that would derive from the introduction of flotation? Refined copper is worth 14 cts. per pound.

**Solution.**—For each of the five cases under consideration the following steps are required for a solution of the problem.

1. Determination of recovery according to formula

$$R = 100 \left( \frac{c}{f} \right) \left( \frac{f - t}{c - t} \right)$$

in which  $R$  is recovery and  $c, f, t$  are the assays of the concentrate, feed, and tailing for the metal of interest.

2. Determination of value of each ton of ore to the smelter according to schedule.

3. Determination of value of each ore, per pound of copper, at the mine. This is obtained from (2), after deduction of freight charges, on dividing by the pounds of copper per ton of ore.

4. Determination of value of concentrate per pound of copper in concentrate, by steps similar to (2) and (3).

5. Determination of value of concentrate per pound of copper *in ore*. This is obtained by multiplying (4) by  $R/100$ .

6. Determination of value of ore if concentrated. This is obtained by deducting from (5) the milling cost, in cents per pound of copper.

7. The increment in returns ascribable to flotation is the difference between (6) and (2).

Table 170 presents the results obtained: the increment in returns decreases rapidly as the grade of the ore increases until it vanishes for ore containing about 11 per cent copper.

TABLE 170.—ECONOMICS OF DIRECT SMELTING VS. FLOTATION FOLLOWED BY SMELTING OF COPPER ORES (PROBLEM 3)

	Copper content of ore, per cent	3	5	8	10	12
	Copper content of concentrate, per cent	25	25	25	25	25
	Copper content of tailing, per cent	0.3	0.4	0.5	0.6	0.7
Step 1	Recovery, per cent	91.0	93.5	95.5	96.5	97.5
Step 2	Value of ore at smelter, dollars per ton	-0.60	+3.40	9.40	13.40	17.40
Step 3	Value of ore at mine per pound of copper, cents	-2.31	+1.40	4.62	5.70	6.40
Step 4	Value of concentrate at concentrator per pound of copper in concentrate, cents	7.48	7.48	7.48	7.48	7.48
Step 5	Value of concentrate at concentrator per pound of copper in ore, cents	6.80	7.00	7.15	7.22	7.30
Step 6	Value of ore if concentrated per pound of copper in ore, cents	2.64	4.50	5.59	5.97	6.26
Step 7	Increment in returns ascribable to flotation, per pound of copper in ore, cents	4.95	3.10	0.97	0.27	-0.14

Graphic solution (Fig. 132) permits accurate determination of the cut-off between concentrating and smelting ore.

The dividing point between shipping ore and concentrating ore is affected but little by the market price for copper. In this example the dividing point occurs at  $10\frac{1}{2}$  per cent copper in the case of an 18-ct. market, at 11 per cent copper in the case of a 14-ct. market, and at 12 per cent in the case of a 10-ct. market.

**Problem 4.**—A series of similar straight-lead ores contain respectively, 20, 25, 30, 35, 40, 45, and 50 per cent lead. If a 90 per cent recovery is obtained from each ore, the grade of flotation concentrate is 65, 67.5, 70, 72.5, 75, 77.5, and 80 per cent lead, respectively. Freight is nil.

Dressing cost is \$1.50 per ton of ore. Lead at 4 cts. per pound. There is no appreciable amount of zinc.

What is the increment in returns derived from flotation, expressed in cents per pound of lead in ore?

**Solution.**—For each of the cases under consideration the following steps are required.

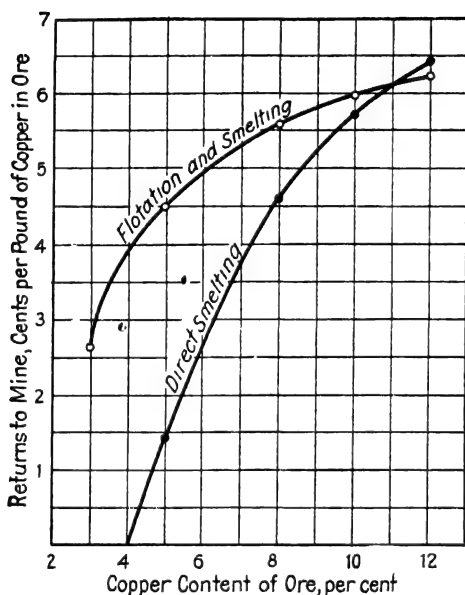


FIG. 132.—Returns from direct smelting, also from smelting following flotation. Copper ores (California schedule, problem No. 3).

1. Determination of the value of the various ores, if smelted directly, in dollars per ton of ore. From this, the value in cents per pound of lead can be obtained.

2. Determination of the value of the various concentrates in dollars per ton, and in cents per pound of lead contained.

3. Determination of the value of the various concentrates, in cents per pound of lead in the ores from which they have been made. This results from a multiplication of (2) by  $R/100$  ( $R$  being the recovery).

4. Determination of the dressing cost per pound of lead in the ore.

5. Determination of the value of the various ores if floated ahead of smelting. This is obtained by subtraction of (4) from (3).

6. The increment in returns ascribable to flotation is the difference between (5) and (1).

Table 171 and Fig. 133 present the results obtained. From the table or the figure it appears that the point of cut-off between

TABLE 171.—ECONOMICS OF DIRECT SMELTING VS. FLOTATION FOLLOWED BY SMELTING OF LEAD ORES (PROBLEM 4)

Step	Lead content of ore, per cent . . . . .	20	25	30	35	40	45	50
	Lead content of concentrate, per cent	65	67.5	70	72.5	75	77.5	80
	Recovery of lead in concentrate, per cent	90	90	90	90	90	90	90
1	Direct-smelting value of ores per pound of lead in ores, cents . . . . .	0.65	1.08	1.37	1.58	1.72	1.80	1.95
2	Smelter value of concentrate per pound of lead in concentrates, cents . . . . .	2.09	2.12	2.14	2.16	2.18	2.20	2.22
3	Smelter value of concentrates per pound of lead in ores, cents . . . . .	1.88	1.90	1.92	1.94	1.96	1.98	2.00
4	Dressing cost per pound of lead in ores, cents . . . . .	0.38	0.31	0.25	0.22	0.19	0.17	0.15
5	Flotation-and-smelting value of ores per pound of lead in ores, cents . . . . .	1.50	1.59	1.67	1.72	1.77	1.81	1.85
6	Increment in returns ascribable to flotation, per pound of lead in ores, cents . . . . .	0.85	0.51	0.30	0.14	0.07	-0.05	-0.10

direct smelting and flotation followed by smelting is at about 42 per cent lead.

In the above problems the dividing points between flotation and direct smelting may appear much higher than is usual in

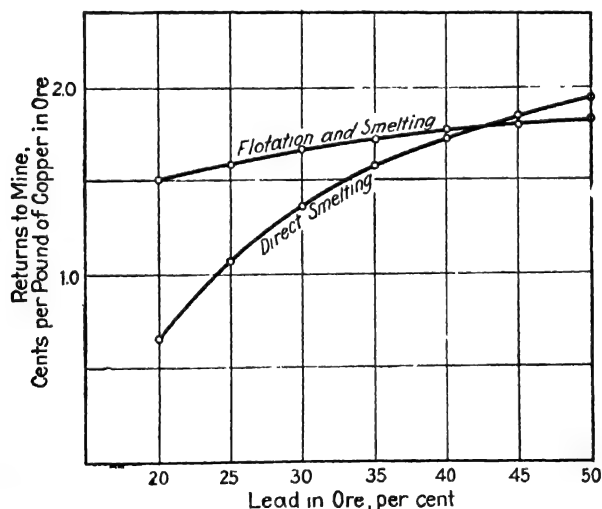


FIG. 133.—Returns from direct smelting, also from smelting following flotation lead ores (Bunker Hill and Sullivan schedule, problem No. 4).

practice. This is because ores containing one valuable metal only were considered and because "open" (*i.e.*, public) smelter schedules were used. If minor valuable metals are present,

and actual smelter contracts are considered, the point of cut-off between direct smelting and flotation before smelting may come at a substantially lower major-metal content in the raw ore. However, the principles of the determination of the metal content at which equivalence between direct smelting and flotation followed by smelting obtains are the same in all cases.

**Effect of Grade of Concentrate and Corresponding Recovery.**—Grade of concentrate and recovery are related inversely: as the

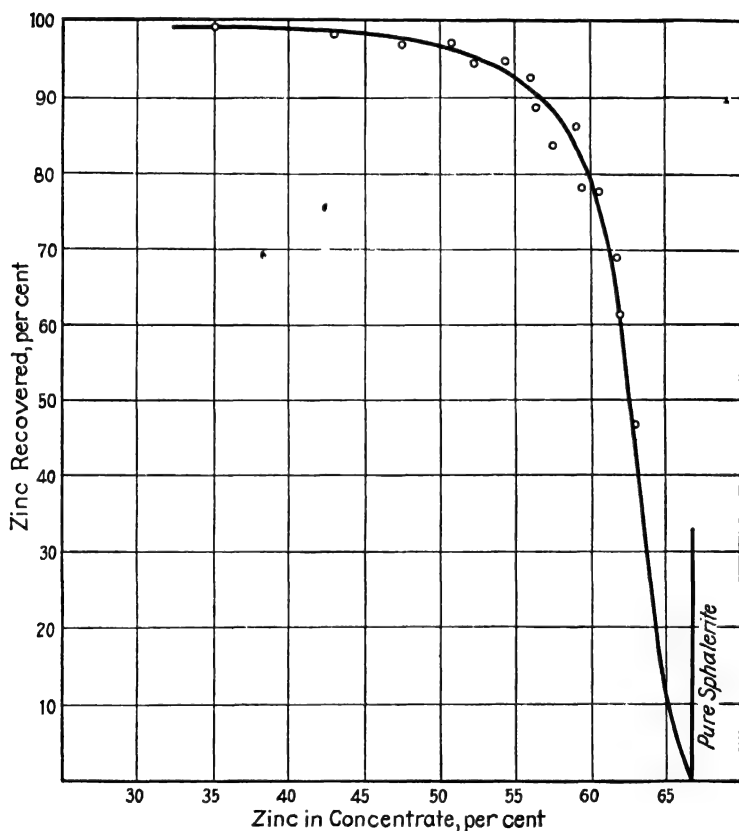


FIG. 134.—Relation of recovery to grade of concentrate.

grade of the concentrate is increased recovery is decreased—that is, if chemical conditions are the same and the variations are obtained by small changes in reagent quantities or by changes in air supply or in the number of cleaning steps. The same relationship between grade and recovery is common to all



concentrating operations. In flotation work, the rate of change of recovery with grade is small until the grade approaches that of the pure mineral whose flotation is desired. From that point on, the rate of change of recovery with change in grade of concentrate is very rapid. This is the essential difference in the

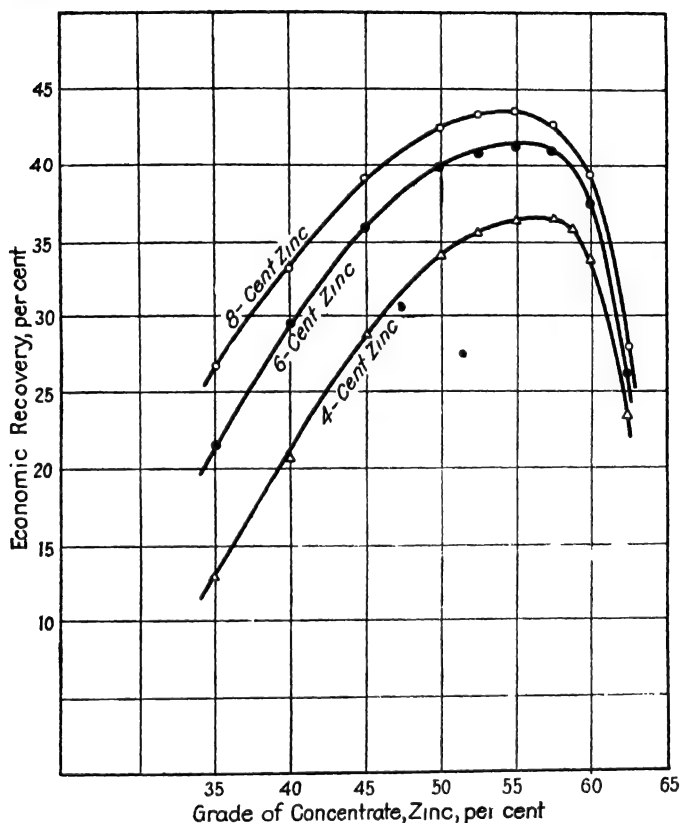


FIG. 135.—Relation of economic recovery to grade of concentrate for various prices of zinc.

(Special case also considered in Fig. 131.)

grade-recovery relationship between flotation and gravity concentration. The general character of the grade-recovery relationship is shown by the data presented in Fig. 134, which pertain to flotation results obtained in the treatment of a zinc ore (9.6 per cent zinc as sphalerite) containing pyrite.

On the basis of the percentage ratio of smelter payments to gross metal value of the concentrate (Fig. 131) and of the recov-

ery-grade curve (Fig. 134), it is possible to deduce net proceeds for various grades of concentrate by simple multiplication. The results obtained (Fig. 135) state the percentage ratio of smelter payment for concentrate to gross metal value of the ore. The points on the curves are a measure of the economic performance. The ordinate, which combines recovery and grade of the concentrate (in the form of receipts from a hydroelectrolytic refinery), gives the net return per pound of metal *in the ore*, that corresponds to the production of various concentrates.

Figure 135 shows that there is a definite grade of concentrate which yields the highest receipts. This grade, in the instance under consideration varies somewhat with the price for zinc—from 54.5 per cent for 8-ct. zinc to 57 per cent for 4-ct. zinc.

The concentrate grade of optimum returns per pound of metal in the ore should be determined in considering the effects of grade of concentrate and of recovery on the dividing point between direct smelting and flotation followed by smelting. Comparison between (a) the ratio of smelter returns from raw ore to gross value of metals in ore, for direct smelting, and (b) the ratio of smelter or hydroelectrolytic-plant receipts from concentrate to gross values of metals in ore, for flotation followed by smelting, allows a choice to be made between the two treatment methods.

**Effect of Cost of Shipping Feed and Concentrate.**—As shipping cost does not increase nearly as fast as the value of the product shipped, it is less per unit of metal if the metal is shipped as concentrate than if it is shipped as ore. Low freight costs therefore favor direct smelting but high freight costs favor flotation before smelting. This effect is more noticeable in the case of lead and zinc than of copper.

### CUSTOM FLOTATION PLANTS

Custom flotation plants are generally erected in a central location to treat the ores from a number of small mines. Often they have a source of rather constant supply amounting to perhaps one-half or more of their average tonnage. This insures enough ore to run the mill.

**Design of Custom Concentrators.**—As contrasted with the arrangement in series which is adopted in many medium-size plants, a favorite arrangement of custom plants is the arrangement in parallel from the fine ore bins ahead of fine grinding to

the concentrate thickeners. This permits milling different ores in several sections. It amounts, in substance, to operating several small mills under one roof at the per-ton cost of a large mill.

One feature of custom plants, which is not generally found in plants treating a uniform ore, is the extensive use of fine-ore bins not only for storage, but with facilities for blending the ores.

The use of blending facilities, of flexible arrangements in the flotation division, and the polysectional grouping of the flotation units fit a plant for treatment of ores covering a greater range of variation than would be possible with the slightly more economical type of plant that does not have these qualifications. In other words, a slightly increased capital cost has extended considerably the applicability of a plant to various ores.

In spite of particular flexibility in custom-plant installations, all ores are not equally treatable in a given plant—at any rate the best results will be obtained only on ores belonging to a certain general group. If the tonnage of a certain ore is sufficiently large, it may of course be possible to modify one section of a custom concentrator to make it treat that ore, but conditions of that sort are the exception rather than the rule.

**Custom Concentrators vs. Small Individual Mills.**—Operating costs of custom flotation concentrators are higher than those of flotation plants treating the same tonnage of a uniform and similar ore: custom plants have to meet increases in certain classes of costs as well as a number of expenditures foreign to usual flotation plants. Special costs are those of purchasing the ore, of service and advice to small mines, and of testing the many ores submitted for purchase. Increased costs derive from the slightly higher capital costs, from the larger amount of analytical work, and from the necessity for greater operating scrutiny in the grinding and flotation divisions.

Although the costs (operating and overhead) of custom concentrators compare unfavorably with those of plants of the same size that are operating on a single ore, their costs are lower than those of the smaller individual plants which would have to be built in their place. Also, the very fact that custom concentrators are buying ores and selling concentrates *makes it necessary*, for them, *to show a profit*. Small mills are not in a position to employ such competent superintendents and metallurgists as those employed in large custom mills, and furthermore the fact that they do not buy ore from mines to sell concentrate to the

smelter does not place upon the operators the same pressure to operate most efficiently. Consequently, metallurgical results are not so good in small individual mills as in large custom mills.

Shipping cost to custom concentrator and the profit which the custom concentrator charges for its service, on the one hand, and lessened capital investment, lowered operating costs, and increased metallurgical efficiency, on the other, are the basic factors involved in a choice between shipping to a custom concentrator and building a mill to treat the output of a small mine.

Viewed in a different way, the choice between shipping to a custom flotation plant, and building a mill is influenced by a number of considerations. The following favor building an individual flotation plant:

- a. Large tonnage of ore.
- b. Constant character of ore.
- c. Long haul to smelter.
- d. Lack of competition between custom flotation plants.
- e. Low grade of ore.

Conversely, if the tonnage of ore is uncertain and its output spotty, if the mining company has small financial means, if it is located reasonably near a custom concentrator, and if the ore is fairly high grade, it will generally be sound business to ship to the custom plant.

**Custom-concentrator Ore Purchases.**—Custom flotation concentrators purchase ore much in the same way as smelters do, but there is a great variation in the schedules, even in the case of

TABLE 172.—TYPICAL CUSTOM-CONCENTRATOR SCHEDULE FOR LEAD-ZINC ORES

**Payments:**

*Gold.*—Pay for 70 per cent of the metal, if ore contains over 0.01 oz. per ton, at \$19.00 per ounce.

*Silver.*—Pay for 70 per cent of the metal, if ore contains over 1 oz. per ton, at New York quotation.

*Lead and Copper.*—Pay for 70 per cent of the lead plus copper (dry assay, or wet assay less 1.5 per cent), if ore contains over 3 per cent, at New York quotation for lead less 2 cts. per pound.

*Zinc.*—Pay for 65 per cent of the metal, if ore contains over 5 per cent, at 40 per cent of the St. Louis quotation.

**Charges:**

*Treatment.*—\$3.00 per ton.

analytically similar ores, because of the many variations that affect the metallurgical results and costs of the flotation operation.

A typical schedule is presented in Table 172(2)(5).

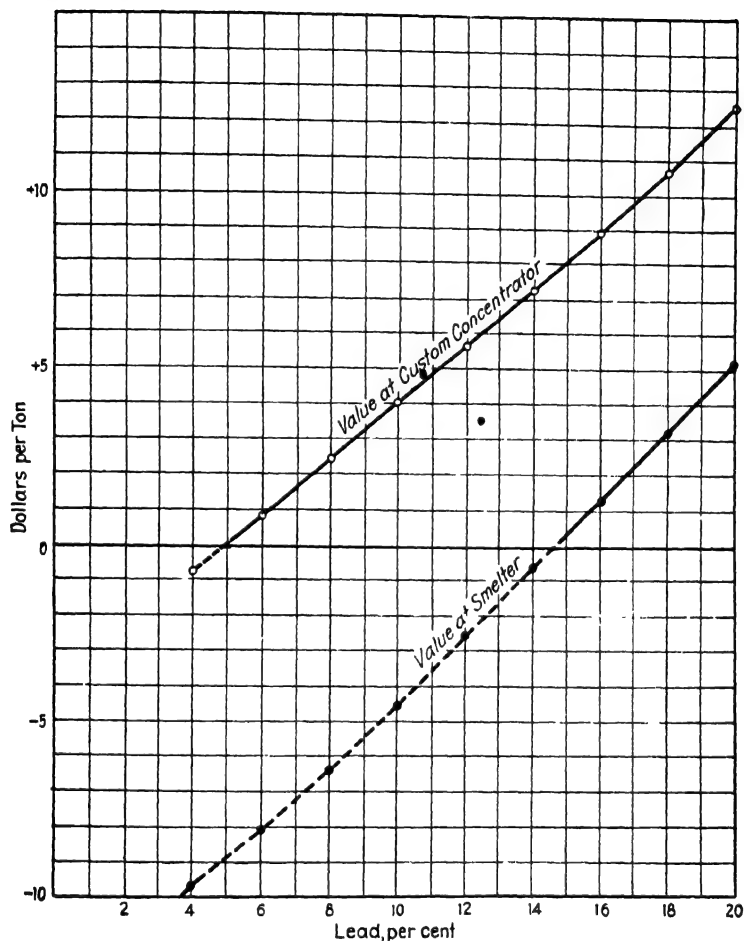


FIG. 136.—Comparison of the value of lead ores to custom concentrator and to lead smelter.

Ores assumed to contain zinc as  $\text{ZnS}$  and iron as  $\text{FeS}_2$  each in amount equal to the lead as  $\text{PbS}$ ;  $\frac{2}{3}$  of the balance is assumed to be insoluble. Midvale open schedules. Lead at 6 cents per pound; zinc at 5 cents per pound.

**Direct Smelting vs. Shipping to Custom Concentrator<sup>(1)</sup>.**—The dividing point between shipping to a custom concentrator or to a smelter is obtained much in the same way as the dividing point between concentrating and shipping to a smelter. In this case

the comparison is made more directly between the returns from two schedules.

Figure 136 has been drawn from the Midvale schedule<sup>(5)</sup> for a lead-zinc-iron ore containing equivalent amounts of the three

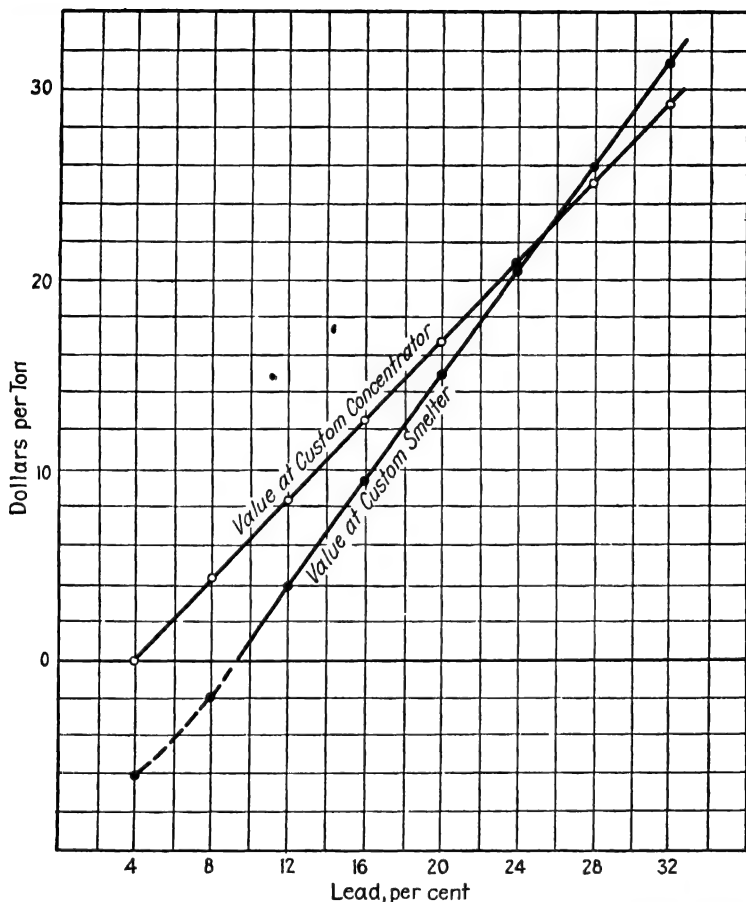


FIG. 137.—Comparison of value of complex ores to selective-flotation custom concentrator and to lead smelter.

Ore is assumed to contain 1 ounce of silver, 10 pounds of zinc and 10 pounds of iron (as sulfides) for each 20 pounds of lead; one-half of the balance is assumed to be insoluble. Midvale open schedules. Lead at 6 cents per pound, zinc at 5 cents per pound and silver at 50 cents per ounce.

metals as sulfides. Likewise Fig. 137 has been drawn for a lead-zinc-iron-silver ore containing half as much zinc and iron as lead, and 1 oz. of silver for each 20 lb. of lead.

In the case of the ores considered in Fig. 136, the value at the smelter is so much lower than at the custom flotation plant that it would pay to concentrate any of the ores in the series. In the case of the ores considered in Fig. 137 it would not pay to ship to the smelter unless the ore contained 25 per cent lead or more. Ores similar to those considered in Fig. 137, but with higher relative amounts of silver, show the dividing point between shipment to smelter and to custom concentrator to have shifted to a lower lead content. For example with 2 oz. silver per ton for each 1 per cent lead, equivalence of schedules takes place at about 19 per cent lead. Conversely, if there is no silver in the ore, it pays to ship to concentrator for all grades of ore.

It has already been stated that custom-concentrator schedules are liable to considerable variation from ore to ore. The custom schedule given above applies to sulfide ores only; for oxidized ores the scale of payments would be lower and treatment charges higher, at the same time as smelter schedules would be somewhat more advantageous (in the case of lead ores, at least). The dividing point between shipping to smelter and to custom concentrator occurs therefore at a substantially lower metal content in the case of oxidized ores.

### CHOICE BETWEEN FLOTATION AND LEACHING

Great hopes were held by champions of leaching for that process of ore treatment. Their hopes have not materialized because the competition between concentration and leaching has been changed by the introduction of flotation. The only fields of application in which leaching competes with flotation are in the handling of oxidized or of partly oxidized base-metal ores and that of precious-metal ores.

As compared with flotation, leaching involves a higher first cost, similar power and labor costs, and a higher cost for supplies. On the other hand, the product from leaching, whether it be solution to be electrolyzed or a precipitate from the leach, is more nearly finished than flotation concentrate. On oxidized copper ores, leaching yields a lower residue than flotation; it is therefore generally adopted.

The possibilities of treating semioxidized ores by a combination of flotation and leaching do not seem to have been fully appreciated.

### TREATMENT OF PRECIOUS-METAL ORES

Choice between flotation, cyanidation, amalgamation, or a combination of these methods of recovering precious metals depends primarily on the character of the ore, but also on the cost of treatment, and on the distance to smelter or refinery.

**Character of the Ore.**—Amalgamation is suited only for the recovery of coarse free precious metals, particularly gold. Cyanidation is best adapted to the extraction<sup>(3)</sup> of fine freed or partly freed native precious metals and to some extent of silver in oxidized minerals. Flotation is suited primarily for the recovery of sulfide, selenide or telluride precious metals, of native precious metals associated with or included in sulfide base metals, and to a lesser extent for the recovery of oxidized silver minerals.

Amalgamation is rarely the only process employed because ores in which the gold recovery by amalgamation is sufficient to compete with the more elaborate processes are the exception rather than the rule.

Cyanidation and flotation are more directly in competition except for (a) ores high in copper which cannot be treated by cyanidation because of the high cyanide consumption caused by the copper minerals; (b) ores high in lead or zinc which are better treated by flotation because of the recovery of the base metals made by flotation and non-recovery made by cyanidation; and (c) oxidized ores in which gold particles are finely disseminated through oxidized minerals and therefore not amenable as yet to successful flotation.

In the ores in which cyanidation and flotation are more directly in competition, cyanidation is favored by coarse dispersion of the precious metals in the sulfides (this results in the exposure of the precious metals to the cyanide solutions) or by the existence of free fine native precious metals. Conversely, flotation is favored by fine dispersion of the precious metals in the sulfides, or if the precious metals occur as sulfides, selenides, tellurides, arsenides, antimonides, sulfarsenides, or sulfantimonides. High grade of ore favors cyanidation because of the lower tailing made.

**Cost of Treatment.**—Operating cost is least for treatment by amalgamation, as the process involves less grinding or supplies. It is highest for cyanidation because of the fine grinding that has to be practiced, and because of the relatively large consumption of cyanide, if measured in terms of flotation reagent consumption.



First cost, likewise, is least for amalgamation and highest for cyanidation on account of the large amount of grinding, thickening, and filtering equipment needed for cyanidation.

The high first cost of cyanidation plants indicates that cyanidation is at a material handicap in comparison with flotation, unless a large body of ore assuring long plant life is available. The low first cost of amalgamation makes this process particularly valuable as a pioneer process for the treatment of ores in remote places, in their earliest stages of development.

**Distance from Smelter.**—Since cyanidation and amalgamation yield a much more concentrated product than flotation, shipping costs are lower than on flotation concentrates. If the haul is sufficiently long, particularly if a railroad or the sea is not available, shipping costs may be the deciding factor between flotation and cyanidation—in favor of the latter.

The following problem illustrates the importance of some of the considerations mentioned above.

**Problem 5.**—A gold ore containing gold, 0.48 oz. per ton; silver, 2.0 oz. per ton; lead, 0.05 per cent; and iron, 2.5 per cent, yields a 96 per cent extraction of the gold and a 30 per cent extraction of the silver by cyanidation. Flotation concentrate contains gold, 7.20 oz. per ton; silver, 25.8 oz. per ton; lead, 7.4 per cent; iron, 36 per cent; copper, 0.8 per cent; sulfur 40.2 per cent; zinc, 1.2 per cent; and insoluble, 6 per cent. Gold recovery by flotation is 94 per cent.

First cost of cyanide plant would be \$1000 per ton of ore—of flotation plant \$600 per ton of ore. Ore reserves are good for 8 years, and there are 350 working days per year.

Operating cost of cyanide plant would be \$1.75 per ton of ore—of flotation plant \$1.25 per ton of ore.

Haul to smelter costs \$3 per ton of dry concentrate. Lead is worth 6 cts. per pound; copper, 13 cts. per pound; silver, 50 cts. per ounce. Should flotation be adopted?

**Solution.**—Determination of the following is required.

1. Average yearly amortization costs (interest on investment plus depreciation) per ton daily capacity; this equals one-half the interest charge in the first year plus the ratio of total cost to years operating.

2. Amortization costs per ton; this is item 1 divided by the number of working days.

3. Total cost (capital plus operating).

4. Value of bullion per ton of ore.

5. Value of concentrate per ton of concentrate.

6. Ratio of concentration

7. Value of concentrate per ton milled.
8. Net returns to mine by deduction of 3 from 4 and 7, respectively. Results are presented in Table 173.

TABLE 173.—ECONOMICS OF CYANIDATION VS. FLOTATION OF A PRECIOUS-METAL ORE (PROBLEM 5)

Step	Economic items	Cyanidation	Flotation
1	Annual amortization cost, per ton daily capacity, dollars . . . . .	155 00	93.00
2	Amortization cost, per ton treated, dollars	0 44	0.26
3	Total cost, per ton treated, dollars . . . . .	2.19	1 51
4	Value of bullion, per ton of ore, dollars .	9.82	
5	Value of concentrate, at concentrator, per ton of concentrate, dollars . . . .	.. ..	142 82
6	Ratio of concentration . . . . .	.	15 96
7	Value of concentrate, at concentrator, per ton of ore, dollars	.. ..	9.14
8	Net returns, per ton of ore, dollars .	7 63	7 63

From the fact that flotation and cyanidation are at a stand-off under the circumstances considered we may conclude that flotation should be favored if there are reasonable prospects for the making of a higher grade concentrate, if the lead and silver markets are likely to rise, or if base metals are likely to become more abundant with depth of ore body.

The critical importance of haul to smelter is well brought out in the above example: a cost of \$6.00 for concentrate shipment advantages cyanidation by 19 cts. per ton treated, and a disappearance of shipping cost advantages flotation by the same amount.

**Combination Treatment Schemes.**—Since amalgamation, cyanidation, and flotation are suited to the treatment of different ores, the joint use of any two of them, or of all three, may result in profitable increased extractions.

Installation of amalgamating plates in combination with flotation or cyanidation entails a small additional first cost or operating cost. If any substantial portion of the gold is recoverable by amalgamation, that process should be added to flotation or cyanidation.

Combination of flotation with cyanidation can be made in several ways: (1) cyanidation of the pulp and flotation of the

cyanide tailing; (2) flotation of the pulp and cyanidation of the flotation tailing; (3) flotation of the pulp, grinding or roasting of the concentrate, and cyanidation of the ground or roasted concentrate with or without cyanidation of the tailing.

Methods 1 and 2 yield equivalent total extractions, Method 1 putting a larger portion of the precious metals in bullion form, at a higher supply cost (cyanide consumption) and at the risk of some difficulty in floating the sulfides from the cyanided pulp. Method 3 is particularly adapted to the treatment of ores in which the precious metals are finely dispersed in sulfides or in a form that is not directly cyanidable.

### CHOICE BETWEEN FLOTATION AND GRAVITY CONCENTRATION

The vast number of gravity concentrating plants that are being remodeled into flotation plants or scrapped to make way for flotation plants suggests that gravity concentration is so obsolete as to make an inquiry into its possibilities hardly necessary. Yet that is not always the case.

In the treatment of oxidized base-metal ores, for the recovery of gold-bearing pyrite from otherwise demetallized pulps, and for the clean-up of coarsely ground flotation tailings gravity concentration is sometimes a low-cost adjunct to flotation. Even though the field of application of gravity concentration in connection with flotation is being restricted every year by the advances in the technology of the newer process, the joint use of the two processes is still worthy of study.

In the treatment of non-metallics, flotation is a newcomer and its applications are restricted. Gravity concentration and hand-picking hold the field. In this instance, just as in the treatment of ores for which flotation appears obvious, thorough prospecting of the possibilities of the minor process should be made.

Operating costs for gravity concentration are slightly lower than for flotation but the recoveries and grades of concentrates are not so good. The poorer metallurgy of gravity concentration results in part from the less perfect liberation resulting from the coarser grinding. But the more important factor seems to be the narrower margin for selection between dissimilar mineral species, a factor that derives from the inalterable relation of specific gravities as compared with the highly modifiable relation of surface polarities of the minerals.

### CHOICE BETWEEN SEVERAL FLOTATION ALTERNATIVES

Choice between several flotation alternatives is necessary in the treatment of certain ores whose mineralogical composition is such that returns from the concentrate or concentrates are comparable by the different treatment schemes. Broadly, the choices are:

1. Collective flotation *vs.* selective flotation, the latter making a concentrate of one metal and discarding the other metal in the tailing.

2. Selective flotation making two concentrates *vs.* selective flotation making a concentrate of one metal and discarding the other metal in the tailing.

3. Collective flotation *vs.* selective flotation, the first making one salable concentrate containing at least two metals and the latter making two or more concentrates.

In Case 1 the factors involved are the extra cost of selective flotation, the increment in returns from the sale of a more concentrated product, and the lessened recovery in the selective concentrate. In Case 2 the factors involved are the cost of recovering the second metal from the tailing of the first operation, and the returns from the sale of the second concentrate. In Case 3 the factors involved are the extra cost of selective flotation over collective flotation, and the increment in returns from the segregated products as compared with those from the collective concentrate.

In problems of the first type the principal variable is the ratio of the mineral to be rejected (if selective flotation is used) to the mineral to be collected. In problems of the second type, the essential variables are the content of second metal in the partly demetallized pulps, and the market price for that metal. In problems of the third type the essential variable is the ratio of the two major metals in the collective concentrate and the appreciation in value of each if separated from the other. The importance of these variables is illustrated by the following problems.

**Problem 6.**—From a series of ores containing 2.5 per cent copper as chalcocite and varying amounts of pyrite it is possible to obtain a 96 per cent recovery of the sulfides in a collective concentrate containing 10 per cent non-sulfides (5 per cent insoluble). The iron content of the feed in the various cases is 8, 6, 4, 3, 2, 1.5, 1.0, and 0.5 per cent. By selective flotation a concentrate having half again as high a non-sulfide

(and insoluble) content can be made with an extraction of 93 per cent of the copper and a rejection of 80 per cent of the iron. Milling cost by collective flotation is \$1.00 per ton; by selective flotation, \$1.10. What is the increment in returns per pound of copper which would result from substitution of selective flotation for collective flotation? Copper at 13 cts. per pound.

**Solution.**—The various steps involved are as follows:

A-1. Calculation of the pyrite, chalcocite, and total sulfide content of each ore.

2. Calculation of the copper content of each collective concentrate (from the sulfide content of the concentrates, sulfide and copper content of the ores).

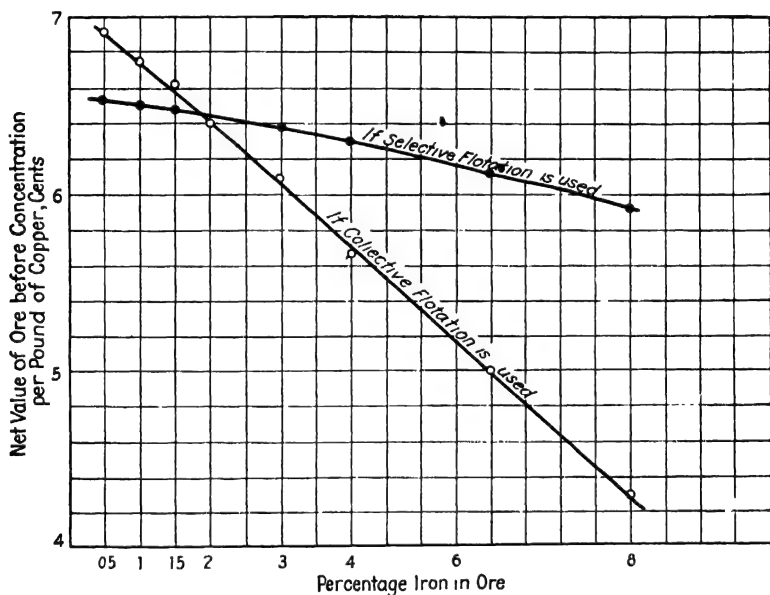


FIG. 138.—Comparative returns by selective flotation and by collective flotation from a series of copper ores.

Ores assumed to contain copper (2.5 per cent) as chalcocite together with varying amounts of iron as pyrite (problem No. 6).

3. Determination of the value of each collective concentrate per ton of concentrate (after, *e.g.*, schedule A in "Handbook of Ore Dressing") and per pound of copper contained in the corresponding ore.

4. Deduction, from (3), of the collective flotation cost in cents per pound of copper, obtaining net value of ore, if floated collectively.

B-5. Determination of the ratio of the iron recovered to that of copper recovered.

6. Calculation from (5), by steps similar to (1) and (2), of the copper content of each concentrate.

7. Determination from (6), by a step similar to (3), of the value of each selective concentrate per ton of concentrate, per pound of copper contained in the concentrate, and per pound of copper contained in the ore.

TABLE 174.—ECONOMICS OF SELECTIVE VS. COLLECTIVE FLOTATION OF A COPPER ORE (PROBLEM 6)

	Iron content of ore, per cent							
	8	6	4	3	2	1.5	1.0	0.5
<b>A. Collective Flotation</b>								
Step 1.								
Pyrite content of ore, per cent	17 12	12 82	8 56	6 41	4 28	3.21	2.14	1 07
Chalcocite content of ore, per cent	3 13	3 13	3.13	3 13	3 13	3 13	3 13	3.13
Total sulfide content of ore, per cent	20.25	15 95	11 69	9.54	7 41	6 34	5.27	4 20
Step 2.								
Copper content of concentrate, per cent	11 1	14 1	19 1	23.6	30.3	35.4	42.8	53.6
Step 3								
Value of concentrate, cents per pound of copper in concentrate	6 58	7 31	7 98	8 42	8 75	8 99	9.12	9.30
Value of concentrate, cents per pound of copper in ore	6.29	7 00	7 65	8 08	8 39	8 61	8 74	8.92
Step 4								
Flotation cost, cents per pound of copper in ore	2.00	2 00	2 00	2 00	2 00	2 00	2 00	2.00
Net value of ore, cents per pound of copper	4 20	5 00	5 65	6 08	6 39	6 61	6 74	6.92
<b>B. Selective Flotation</b>								
Step 5								
Ratio: iron recovered	20	20	20	20	20	20	20	20
copper recovered	93	93	93	93	93	93	93	93
Step 6								
Copper content of concentrate, per cent	31 1	36 1	42 5	47 0	52 4	55.4	59 2	63.0
Step 7								
Value of concentrate, cents per pound of copper in concentrate	8 75	8 95	9 13	9 22	9 27	9 31	9 36	9 40
Value of concentrate, cents per pound of copper in ore	8 12	8 31	8 48	8 56	8 61	8 65	8 70	8 73
Step 8								
Flotation cost, cents per pound of copper in ore	2 20	2 20	2 20	2.20	2 20	2.20	2.20	2.20
Net value of ore, cents per pound of copper	5 92	6 11	6 28	6 36	6.41	6 45	6.50	6.53
Step 9.								
Increment in returns by selective flotation in place of collective flotation, cents per pound of copper in ore	1.63	1 11	0.63	0.28	0.02	-0 16	-0.24	-0.39

8. Subtraction from (7) of the cost of treatment by selective flotation, in cents per pound of copper. This yields the net value of the ores if floated selectively.

9. Comparison of the results in (4) and (8).

The results obtained are presented in Table 174 and Fig. 138.

It is seen that equivalence in economy is reached for an iron content in the feed of about 1.9 per cent.

**Problem 7.**—Treating a lead-zinc ore, a flotation plant makes a lead concentrate but discards the zinc in the tailing. Installation of a zinc-recovering division would involve a first cost of \$150 per ton of deleded ore treated daily. Operating costs would be increased by \$0.25 for each ton of deleded ore treated. Recoveries of 40, 50, 60, 65, and 70 per cent of the zinc in the deleded pulp can be made in a 55 per cent concentrate (containing lead, 6 per cent; silver, 3 oz. per ton; insoluble, 3 per cent) if the zinc content of the deleded pulp is 2.0, 2.5, 3, 4, 5 per cent. What is the lowest zinc content at which the operation would be profitable enough to repay the cost of installation in 2 years with zinc at 4, 5, and 6 cts. per pound, lead at 6 cts. per pound, silver at 50 cts. per ounce? Freight to hydroelectrolytic plant is \$4.00 per dry ton. The plant is operated on an average of 300 days per year.

**Solution.**—If cost of \$150 has to be repaid in 2 years, amortization amounts to  $\$150 \div 0.06 [150 \div 75]$  or \$163.50 for the 2 years, for each ton of daily capacity. Amortization cost per ton is therefore  $\frac{\$163.50}{300 \times 2}$  or \$0.37, and the total cost,  $\$0.37 + 0.25 = \$0.62$ .

The following steps are required in the solution of the remainder of the problem.

1. Determination of the value of the concentrate at hydroelectrolytic zinc refinery, per ton of concentrate.

2. Determination of the value of the concentrate, per pound of zinc, at the concentrator. This is obtained by deducting from (1) the freight on concentrate and dividing the remainder by the pounds of zinc in the concentrate.

3. Determination of the gross return on the proposed operation per ton of deleded pulp. This is obtained from the grade of the deleded pulp and the recovery of zinc made in floating it.

4. Comparison of (3) with the cost of flotation (including 2-year amortization) shows the dividing point between profitable and unprofitable installation.

Returns per ton of deleded pulp are presented in Table 175. Deduction of the cost of recovering the zinc (62 cts.) from the gross returns indicates the profit per ton obtainable from addition of the zinc-recovering division over and above return of investment in 2 years. The algebraic sign of the remainder establishes a demarkation between profitable and unprofitable operation as shown. On 4-ct. zinc

TABLE 175.—ECONOMICS OF INSTALLATION OF ZINC-RECOVERING DIVISION  
IN TREATMENT OF COMPLEX ORE (PROBLEM 7)  
Gross returns per ton of delead pulp, cents

Zinc price, cents per pound	Zinc in delead pulp, per cent				
	2	2 5	3	4	5
4	24	37	54	78	105
5	33	51	73	106	143
6	41	65	93	134	181
Unprofitable			Profitable		

a 3.4 per cent zinc content is required for the operation to be profitable. The minimum profitable zinc content is reduced to 2.7 per cent on a 5-ct. market, and to 2.4 per cent on a 6-ct. market.

**Problem 8.**—A plant handling 500 tons of lead-zinc ore per day makes 100 tons daily of a 52 per cent zinc concentrate containing 4 per cent lead, 4 oz. of silver per ton, and 6 per cent insoluble. It is found that by grinding the concentrate and floating again a finished concentrate containing 58 per cent zinc, 4 per cent lead, 4 oz. silver per ton, and 3 per cent insoluble can be made. The operating cost of the additional operation is \$0.40 per ton of primary concentrate, the first cost of the installation \$15,000, and the recovery of zinc in the final concentrate 95 per cent of that in the primary concentrate. Zinc at 5 cts. per pound, lead at 6 cts. per pound, silver at 50 cts. per ounce. How much time would be required to pay for the installation? Freight on concentrates is \$3.00 per wet ton; concentrates contain 10 per cent moisture.

**Solution.**—If the cost of installation of regrinding and refloating division is to be repaid in  $x$  days, the amortization cost is  $15,000/x$  dollars per day, and the total daily cost is

$$[(0.40) \times (100)] + \frac{15,000}{x} \text{ dollars.}$$

The returns per ton of concentrate (Table 165) are \$19.12 in the case of the primary concentrate, and \$24.67 in the case of the secondary concentrate. Daily returns are therefore \$1912 and  $2467 \times 0.95 \times \frac{5}{8} = \$2100$ , respectively. In the case of the higher grade concentrate, the returns are \$188 higher.

Putting the excess returns to equal the daily cost,

$$40 + \frac{15,000}{x} = 188; x = 99 \text{ days.}$$



**Determination of Optimum Grinding<sup>(6)</sup>.**—As the fineness to which an ore is ground is increased, the liberation of the minerals becomes more perfect and flotation results are bettered, provided overgrinding is not excessive. Returns per ton of ore increase, therefore, as grinding is increased. Conversely grinding cost increases with fineness of grinding. Optimum grinding is that which yields maximum excess of returns over cost of grinding.<sup>1</sup>

## CHAPTER XVIII

### TESTING AND TESTING EQUIPMENT

Flotation testing may be practiced with one of several objects in mind: (a) ore testing, (b) reagent testing, (c) equipment testing, and (d) circuit testing. For the average practicing engineer and custom-concentrator metallurgist ore testing is the commonest; for the average mill man it may be reagent, equipment, or circuit testing. Since the last three involve a comparison between several ore tests, a description of testing for ores will cover in substance all the steps of reagent, equipment, and circuit testing.

The discovery of an ore body requiring concentration does not justify the erection or even the design of a milling plant unless it is reasonably certain that the ore can be treated at a profit. This is ascertained by testing, because the great complexity of ores makes it impossible to predict their responsiveness to flotation except in a rough manner. Flotation testing is more necessary than testing for other processes, such as gravity concentration, on account of the outstandingly delicate properties on which flotation success or failure hinges. Testing answers both technical questions, such as are related to the feasibility of concentration by a certain process, and economic questions, such as mill-return estimates. The recent reduction in the number of costly, large-scale mistakes makes it apparent that judicious flotation testing is a sound investment.

Testing ores for custom milling differs from the usual laboratory testing in that much less latitude is allowed to the operator who must determine whether the new ore will or will not fit into the scheme in use at the custom concentrator.

#### BATCH TESTING

**Steps in Ore Testing.**—The first step in testing an ore is to secure a representative sample<sup>(38)(43)</sup>, and to make thereon a chemical analysis that is sufficiently complete to account for most of the minerals in the ore. Inspection of specimens with or with-

out a hand glass is generally sufficient to determine the principal constituents of the ore, and thus indicate what scope the chemical analysis should cover.

The next step is to determine, with the help of a microscope, the exact mineral make-up of the ore, as well as the structural and textural associations of the minerals. Joint consideration of the chemical, mineralogical, and textural analyses permits of classifying the work on a new ore sample as being routine or not. The work should be considered as routine only when the chemical, mineralogical, and textural analyses resemble those of a well-known ore; when even one of these analyses is distinctly different from experience, the work will involve an unusual amount of original search and will call for considerably more time and supervision by an expert.

The third step is to conduct batch flotation tests along the lines dictated by experience with ores of similar composition and texture.

Once a fairly successful test has been obtained, the results can be improved by 'cut and try' methods, assisted by experience. Small increases or decreases in the quantities of reagents, changes in the pH, in the grinding conditions, in the place of addition of reagents, in the time of contact between reagents and ore, in the extent of aeration during flotation, etc., frequently result in substantial improvements in metallurgical results. Replacement of one reagent by a different reagent having slightly different properties is also a favorite testing artifice.

The importance of proper hydrogen-ion control has been repeatedly emphasized in this book. Formerly it was considered sufficient to determine the reaction of the pulp to litmus before and after reagent addition; this very crude determination of acidity or alkalinity should be replaced by the determination of the pH of the ore pulp.

To determine whether grinding has resulted in sufficient liberation of the minerals, the ground product can be examined directly under the microscope, or else it can be briquetted and the polished briquette examined. This permits of making, respectively, a qualitative estimate or a quantitative determination of the extent of mineral liberation. Comparison of the apparent composition of loose ore particles with that of polished briquettes of these particles may disclose special structural features, such as the presence of slime-coated or crust-covered particles.

Chemical analyses of flotation-test products are required to compute the metallurgical results of the tests; a record of the weights of the products is necessary, as it constitutes a check on the recovery computed from assays only; it should, therefore, not be omitted. In case the results of the flotation operation are not up to expectations, an examination under the microscope should be made of the concentrates and tailing.

Even though complete success is encountered in batch testing, it does not follow that the same proportions of reagents and the same operating conditions will succeed in the continuous operation of a plant. The translation of the results of batch tests to plant practice is a special art.

#### TRANSLATION OF BATCH LABORATORY TESTING TO PLANT OPERATION

Flotation testing by batches is widespread because it is simple, relatively inexpensive and predicts in a broad way the results of plant operation. Indeed, in flotation work, the agreement of large-scale operation with laboratory tests is much better than the agreement between large-scale operation and miniature-scale tests in most chemical, metallurgical, and ore-dressing operations. This is because the number of particles involved, even in a charge as small as 500 g., is so large that the laws of averages hold almost as well as in the field of molecular dynamics.

In spite of the agreement between batch testing and plant operation, there are certain dissimilarities. These dissimilarities are not directly traceable to the flotation operation itself, but rather to inherent differences in the pulp circuits that are used. For crude work the dissimilarities can be ignored, but the introduction of refinements in a plant, as likewise good plant design, require a knowledge of circulating loads which cannot be acquired by batch testing.

A continuous laboratory testing plant permits bridging of the gap between batch testing and plant operation. Such a plant may have a capacity ranging from 25 to 250 lb. of ore per hour, and should be operated several hours under each set of conditions in order to yield significant results.

If a large plant is contemplated, erection of a pilot plant having a capacity equivalent to that of a small mill is a wise investment as it allows the future plant operator to become familiar with the

idiosyncrasies and range of variations of the ore before and during construction of the concentrator. At the same time it disposes in a marketable way of the ore from development of the mining property.

In its most complete development, flotation testing preliminary to the construction of a new plant consists therefore of three stages, each considerably more expensive than the one preceding:

1. Batch testing.
2. Continuous laboratory testing.
3. Pilot-plant testing.

Arrangement of the flotation division of a plant into a number of units in parallel permits direct comparison between different machines, different circuits, or different reagents on an identical feed in a manner more convincing than any yet devised.

**Grinding-classifying Circulating Loads.**—Grinding mills used in open circuit discharge a ground product that has passed through the mill but once. The average time ore particles are in the mill equals, in hours, the ratio of tonnage of solids in the mill to hourly tonnage ground. There are, of course, variations in the duration of grinding to which any one particle has been subjected, but on the whole the range in grinding time is small. In mills operated in closed circuit with classifiers, the average time of grinding is smaller, but the range of time that different particles are in the circuit is larger, as may be observed from the size of the circulating load, that is the number of passes through the mill. In batch grinding all particles are subjected to grinding for the same length of time. Thus batch grinding differs from closed-circuit grinding in the duration of exposure to oxidation, carbonation, and reagents, even if the average grinding time is the same in both cases.

Batch-ground and closed-circuit-ground products differ also in the relative abundance of particles of different sizes. A classifier overflow, such as is generally fed to flotation machines is coarser, on the average, than an unclassified ground product having the same maximum particle size. In other words, there are fewer overground particles and more coarse middling particles in products ground in mill-classifier circuits.

**Circulating Loads in Flotation Division.**—Practically all flotation operations involve the production of one or more intermediate products which are returned to the main circuit at

one point or another. If intermediate products were identical with the new feed at the point of introduction in the circuit, they should behave in the same way, and no substantial circulating load should build up. Thus, if in a series of locked-batch tests a scavenger concentrate were returned with the new feed, and amounted to one-tenth of the first feed, it should give rise, upon again passing through the cell, to a second-pass scavenger having a bulk one-hundredth that of the new feed; and so on. At the end of  $n$  passes, the bulk of the circulating load would be

$$\sum_0^{\infty} \frac{1}{10} + \frac{1}{10^2} + \frac{1}{10^3} + \cdots + \frac{1}{10^n},$$

which is the summation of members of a converging series having one-ninth as limit. Analysis shows that the equilibrium bulk of an intermediate product whose single-pass bulk is

$$\frac{1}{p} (p > 1),$$

is the limit of

$$\sum_0^{\infty} \frac{1}{p} + \frac{1}{p^2} + \frac{1}{p^3} + \cdots + \frac{1}{p^n},$$

or

$$\frac{1}{p-1}.$$

Accordingly, if the composition, particle size, and state of liberation of a circulated product were identical with those of the new feed at the point of introduction in the circuit, the bulk of the circulating load could be calculated from batch tests.

But intermediate flotation products such as scavenger concentrates or cleaner tailings are not like the new pulp to which they are added. Indeed, they contain in greater proportion the difficult particles, that is middling particles, overcoarse and overfine particles of the minerals that are being collected and overfine particles of gangue. Upon refloatation, the circulated material is floated to a different extent from new feed, so that the summation of the series which would yield the equilibrium circulating load should contain terms larger than indicated above. In such a case the series may be convergent or not; at any rate, if convergent, the series would have a higher limit, showing that a larger circulating load would build up.

An increase in circulating load results in crowding the flotation machines, and therefore in the establishment of different flotative

conditions. This, in turn, sets up a different equilibrium bulk for the circulating load.

For the mill operator the disposal of intermediate products is frequently a major problem which is not necessarily solved by hiding the products in sundry places in the main circuit. This explains in part the recent growth of middling grinding before return to the main flotation circuit.

The abuse and not the practice of returning intermediate products to the main flotation circuit is to be condemned. Judicious use of middling returning offers some of the difficult particles an increased opportunity to report in the place where they are desired. Thus a better selection is obtainable than with a simpler circuit.

Since batch testing does not allow the establishment of circulating loads, it does not permit an accurate estimate of the effect of the introduction of intermediate products in the main circuit, nor of the bulk of the circulating load, and therefore of the cell capacity that is needed.

**Continuous Laboratory Testing.**—A continuous laboratory testing apparatus is really a miniature flotation plant. It may consist, for example, of a bin feeding a ball mill in closed circuit with a classifier and of a number of flotation cells arranged in various order, with reagent feeders, conditioning tanks, and pulp thickeners.

Important requirements for a continuous laboratory flotation plant are flexibility of the various units, accessibility for adjustments, quick response to adjustments, sampling facilities at many points, compactness, reasonable first cost, and possibility for thorough cleaning.

Operation of a continuous testing plant differs from that of a batch flotation machine in that the attention of the operator must extend simultaneously to many features instead of being concentrated on one operation. Also, a run of several hours is generally necessary to establish equilibrium, particularly if complex circuits are in use.

Testing in a continuous flotation plant requires a relatively large ore sample (2 to 20 tons) instead of the customary 25- to 200-lb. sample necessary for batch testing.

**Pilot-plant Testing.**—Pilot-plant operation differs from plant operation in two important respects: permissible variations in grinding, reagents, reagent feeding, and circuit "hook-ups" are

much wider, and considerably more trouble should be expected since the object of pilot-plant testing is to discover and straighten out the difficulties. Interpretation of pilot-plant results in terms of plant operation is open to some question only on the score of cost prediction, which it is difficult to make exactly.

#### MICROSCOPE LABORATORY EQUIPMENT AND ITS USE

**Microscopes.**—A low-power binocular microscope is desirable for all-round work. A petrographic microscope is convenient for the study of transparent minerals and for the examination at higher magnification than can be obtained with the binocular microscope. A reflecting metallographic microscope is necessary in the medium- and high-power examination of opaque surfaces for the detection of coatings on sulfides, and for the structural, qualitative mineralogical, and quantitative mineralogical analyses of opaque products. Photographic attachments for the petrographic and the reflecting metallographic microscopes are desirable.

Microscopes can be used to examine specimens by transmitted light, in which case thin sections having a thickness of about 0.03 mm., or crushed fragments spread on a slide (or between a slide and a cover glass) are examined<sup>(23)(33)(52)</sup>. The microscope can also be employed to examine specimens by reflected light, in which case natural surfaces, polished ore fragments, polished briquettes, or loose particles are examined<sup>(34)</sup>.

**Polishing Equipment.**—A special technique is necessary for the preparation of polished sections of ores or briquettes.

The equipment required includes a rock saw<sup>(23)(33)(50)</sup>, grinding wheels, polishing wheels and plates, a briquetting machine, and etching reagents. In a small laboratory the rock saw can be replaced by a simple hacksaw used in conjunction with a vise. Grinding and polishing wheels can be dispensed with at the expense of time used up in the slow polishing of specimens on glass plates and polishing paper. Grinding and polishing wheels can be purchased ready-made, or be made from cast-iron disks<sup>(17)</sup>. Grinding wheels may consist of metal disks 1 in. thick and 10 in. in diameter, screwed on motor-driven spindles 1¼ in. in diameter, revolving at about 750 r.p.m.; polishing wheels are faster revolving metal disks 5 to 8 in. in diameter covered with felt, well-worn canvas, or broadcloth.



**Making Polished Sections.**—Making polished sections is within the reach of one versed in general laboratory technique, provided his attention is directed to a few pitfalls of a general character. The first requirement is to be patient: it does not pay to cut down the polishing time at any one stage in the operation, except at the expense of considerably more time to be spent in the subsequent stages. The second requirement is to eliminate carefully all grit between polishing stages by washing thoroughly, in order to prevent scratching of specimens by contamination of the fine-polishing surfaces. The third requirement, when using a grinding wheel, is to use regularly all the surface of the wheel, which otherwise becomes uneven. Lastly, it should be remembered that too much polishing develops an undue amount of relief, thus obscuring many features of interest. Careful selection of a good sample is wise. Such a sample should be neither too small to be unrepresentative or difficult to hold, nor too large for reasonable polishing time. Pieces having an area of  $\frac{1}{4}$  to  $\frac{1}{2}$  sq. in., a thickness of  $\frac{1}{2}$  to  $\frac{3}{4}$  in., and a nearly flat face have been found convenient.

The spall of ore should first be ground on an emery wheel, or on a coarse-grinding wheel using a water slurry of 48 to 65 mesh carborundum as the grinding medium. During this step, as well as in all subsequent stages, the sample should be rotated gently in the direction opposite to the rotation of the wheel in order to avoid grooving of the specimen by parallel scratches. The edges and corners of the sample should be beveled so as to prevent tearing of the polishing cloth in the final polishing stages. When the surface of the spall is ground flat, it should be washed free of grit and taken down on the next grinding wheel using a slurry of finer carborundum, and so on, until the sample is ready to be polished on a moistened, rouged, cloth-covered polishing wheel. Some microscopists prefer to use "laevigated" or "floated" (elutriated) alumina, which is colorless and harder than rouge (iron oxide). A high polish is rarely necessary; this is fortunate as much care is required in removing the last scratches left by the grinding and polishing powders. A high polish is best obtained on a sample having a small area, and by running the finishing wheel nearly dry.

Thin sections are occasionally needed in connection with flotation testing, particularly in the determination of the gangue minerals in sulfide ores, and in the study of non-sulfide ores.

The technique of preparing thin sections has been described in detail<sup>(17)(26)</sup>.

**Making Briquettes.**—A briquetting machine is indispensable to the well-equipped flotation laboratory. Its recent introduction, together with the poorly known briquetting technique are responsible for a regrettable lack of information as to the necessary extent of grinding in complex ores.

Briquettes consist of comminuted material cemented by a matrix of some such material as plaster of paris, sealing wax, or bakelite. Bakelite, which is a synthetic resin obtained through condensation of phenolic compounds at a temperature of 140 to 200°C., is better suited than other cementing materials because it is non-crystalline, fully as hard as the softer minerals, and sticks to the minerals when properly applied<sup>(16)</sup>. The non-crystalline character of bakelite allows ready discrimination of the groundmass from the imbedded particles; its medium hardness prevents the polishing in relief of many common opaque minerals (with the exception of pyrite) and thus makes easier the identification of very small particles, which otherwise might be substantially unrecognizable (as for example in the softer sealing wax).

Bakelite briquettes can be made by mixing in the cold about equal volumes of ground ore and of bakelite powder, placing the mixture in a mold, and heating on a hot plate for a few hours. This procedure is not recommended because far better results are obtainable with the simple briquetting machine described below. Briquettes made at atmospheric pressure and without careful temperature control are not so satisfactory, because they are porous, because of the softer character of the resulting matrix, and of the poor adherence between particles and matrix.

Figure 139 shows the briquetting machine devised at the research laboratory of the United Verde Copper Company, under the direction of O. C. Ralston, and with the cooperation of R. E. Head of the U. S. Bureau of Mines. The machine consists essentially of a mold which can be heated electrically to 180°C. by means of resistance coils placed in an annular space within the mold casing. The ore-bakelite mixture is placed in the mold and kept there under pressure by a hydraulic jack. In the original United Verde design the jack could exert a pressure of 1.5 tons. However, a briquetting jack capable of developing a pressure of

10 tons is preferable as it yields more compact briquettes. In the type of apparatus just described, the baking is carried on at the same time as pressure is exerted, so that a homogeneous briquette is obtained.

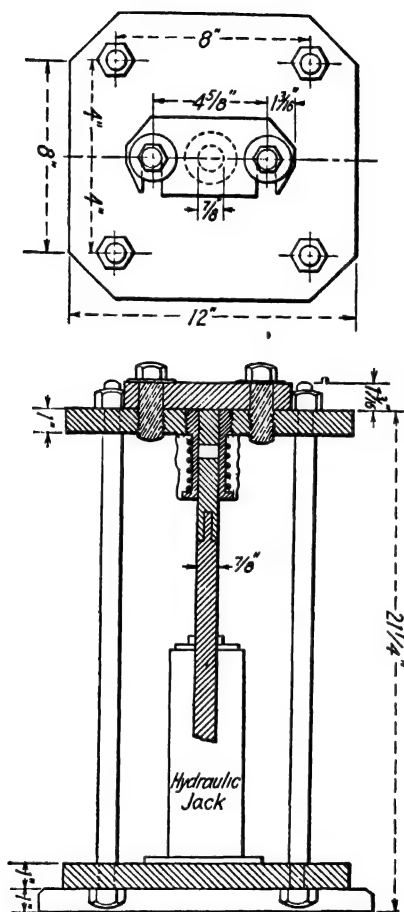


FIG. 139.—Briquetting apparatus.

Briquettes are polished in the same way as ore samples; in fact easier because the briquettes have flat faces and are circular. On the other hand, the small size of the particles that are polished, together with the differences in hardness that always exist between the matrix and some particles, makes it necessary to obtain a higher polish than with ores. This is particularly true

if fine products are examined. In that case it is necessary to restrict the polishing to a small surface and to use particularly fine polishing powders.

The comminuted material used in making briquettes should be sized, closely if possible. This facilitates the estimation of the composition of the sample and makes such an estimation more reliable because variations in particle size enter into the estimates as a lesser factor. In material to be briquetted the presence of particles of colloidal or near-colloidal size is objectionable because these particles adhere to the coarser particles, weakening the bond between them and the bakelite.

**Making Quantitative Mineralogical Analyses.**—Quantitative mineralogical analyses of polished or thin sections can be made by subdividing the field into squares of suitable size through the use of a grid eyepiece, and by estimating the composition of each square in terms of the various minerals which have previously been recognized in that field(8)(33)(34)(52).

Accurate quantitative determination of the constituents of a briquette, or of particles loosely spread on a slide, requires (a) uniform dispersion of the particles; (b) a magnification that is sufficient for clear, instantaneous recognition of the minerals, but not so large that it restricts the number of particles in the field of vision to less than five; and (c) the existence of discriminating traits such as cleavage, relief, or striking color in the various minerals.

In case natural differences in color exist between minerals, a count of the particles belonging to the various mineral species can be made readily; in case there are no natural differences in appearance between minerals, they can be artificially created by etching or staining. For instance cerussite is stained yellow by dichromates in acid solution, whereas calcite and anglesite are not colored; chromates in alkaline solution color anglesite yellow but do not color cerussite or calcite. In the same way, chalcopyrite can be told from pyrite more easily after treating with silver nitrate which imparts to chalcopyrite a bornite-like appearance whereas pyrite remains practically unchanged. Although there is some difference in color between enargite and chalcocite, this difference can be magnified by treatment with nitric acid which colors chalcocite blue. Calcite can be told readily from silicates or from quartz by treatment with ferric chloride which coats it with brown ferric hydroxide.

In making a quantitative determination of the constituents of a flotation product the mineralogical species present and the qualitative composition of middling particles should first be ascertained. This should be followed by a count of the free particles of the various minerals and of the various middling particles together with an estimate of the average composition of each type of middling particle.

Thus, the concentrate obtained from a copper ore composed of chalcopyrite, pyrite, and non-sulfide gangue minerals may contain ternary particles of the two sulfides and gangue, binary particles of the two sulfides and of each sulfide with gangue, and free chalcopyrite, pyrite, and gangue particles. After a determination of the proportion of these seven classes of particles in 1000 or more particles, and by taking into account the density of the minerals (a sized feed is assumed), it is possible to predict the quantity of rejectable gangue or pyrite that does not involve further grinding, the desirability of finer grinding, etc. The actual counting operation does not call for a great outlay of time, but it is hard on the eyes so that but little can be done at one sitting. The complete operation of selecting a sample, sizing it, making a briquette, polishing the briquette, staining the sample, counting the particles, and computing a proximate and structural analysis requires considerable time, particularly if several valuable minerals occur, and if many middling particles complicate the counting.

#### **Correlation of Quantitative Microscopy and Flotation Results.—**

The making of a quantitative determination of the mineralogical composition of a ground product by briquetting, and its correlation with flotation results are exemplified by the following data which were obtained on a complex lead-zinc-iron ore.

The product that was examined consisted of the  $-150 + 200$  mesh (screened) portion of the flotation feed and contained (as determined by chemical analysis): lead, 4.4 per cent; zinc, 10.1 per cent; iron, 11.8 per cent; insoluble, 41.3 per cent. The principal minerals were galena, sphalerite, pyrite, quartz, and feldspar. The results obtained with the microscope (Table 176) were as follows: total number of particles counted and determined, 1523: galena, 31; sphalerite, 139; pyrite, 223; gangue, 1030; mixed particles, 90, of which 3 contained galena and sphalerite, 68 sphalerite and pyrite, and 19 gangue and sulfide, with the gangue predominating.

TABLE 176.—QUANTITATIVE ESTIMATE OF COMPOSITION AND LIBERATION OF A FLOTATION FEED  
MADE BY THE USE OF A MICROSCOPE

Kind of particles	Number of particles	Per cent by volume	Per cent by vol- ume $\times$ density	Per cent by weight	Per cent of the total weight repre- sented by			
					Galena	Sphalerite	Pyrite	Gangue
Total.....	1523	100	329 0	100 0				
Free particles								
Galena ..	31	2 03	15 2	4 6	4.6			
Sphalerite ..	139	9 1	36 4	11.1		11.1		
Pyrite..	223	14 6	73 0	22 2			22.2	
Gangue..	1030	67 6	179 0	54.5				54.5
Middling particles								
Galena sphalerite.....	3	0 2	1 1	0.3	0.2	0.1		
Galena pyrite..	0	0	0	0				
Pyrite sphalerite.....	68	4.45	20.0	6 1		3.0	3.1	
Gangue sulfides, mostly gangue.....	19	1.25	4 35	1.3	0.1	0.2	0.3	0.7
Total.....	.....	.....	.....	.....	4.9	14.4	25.6	55.2

From Table 176 it is seen that the total galena content of the sample is 4.9 per cent, which checks very well with 5.1 per cent, (calculated from the assay, assuming all the lead to be present as the sulfide); similarly, the total sphalerite content is found to be 14.4 per cent against 15.0 per cent, calculated; the total pyrite content, 25.6 per cent, compared with 25.2 per cent (calculating all the iron as pyrite). Of the total lead, over 90 per cent appears free; of the gangue about 99 per cent appears free; of the iron, 87 per cent appears free and 12 per cent tied up with zinc in middling pyrite-sphalerite particles; of the zinc, 77 per cent only appears free, whereas 21 per cent is associated with pyrite. It follows that the recovery of lead in the lead concentrate should be fairly good, that the rejection of gangue should be good, but that the separation of zinc from iron should leave considerable to be desired. In coarser sizes the liberation of the minerals would be still less perfect, but in the finer sizes it should be better. The results of the quantitative mineralogical analysis indicate that it would be advisable to grind the ore finer than 200 mesh, or else to collect a clean zinc concentrate under rather weak flotative conditions, followed by the collection of a zinc-iron middling requiring regrinding and a secondary flotation operation. In agreement with the results of the quantitative mineralogical analysis, it was found on floating a pulp of this ore ground so that 75 per cent was finer than 200 mesh that the coarse portions of the zinc concentrate were higher in iron than the finer portions, and that the recovery of coarse zinc was poor.

When a quantitative determination of the constituents of an elutriated product has to be made, that is, when it is not permissible to consider that the particles of all minerals have the same average size, a satisfactory approximation can be achieved by assuming that the average diameters of the various particles are related in accordance with Stokes' law which states that the diameters  $a$ ,  $a'$  of solid particles settling equally fast in a medium of specific gravity  $d$  are inversely proportional to the square root of the apparent densities  $(D - d)$  and  $(D' - d)$ . Since the masses of particles of the same configuration are proportional to  $Da^3$  and to  $D'a'^3$ , the masses of particles of different specific gravities but of the same settling velocity are as  $D \times (D - d)^{-3/2}$  is to  $D' \times (D' - d)^{-3/2}$ . Thus, galena and quartz particles which settle equally fast in water have masses in the ratio of 1:2.75.

**Errors in Interpretations from Briquettes.**—It is natural to assume that the cross-section of particles obtained by polishing a briquette is representative of the contents of the briquetted material both as to texture and composition. Yet this is not strictly true as there are systematic errors inherent in the method itself.

The most important error is an overestimation of the liberation of the minerals<sup>(29)</sup>. This derives from the fact that a free particle cannot be cut to simulate a middling particle, but that a middling particle can appear as a free particle. Statistical analysis is possible in certain idealized cases. For instance, in the case of a middling particle spherical in shape and consisting of an inner sphere of one constituent surrounded by a shell of the other, the probability of the particle appearing free is  $1 - \frac{r}{R}$ , in which  $R$  and  $r$  are the radii of the outer and inner spheres. Statistical study shows that, other things being equal, the more elaborately interlocked the constituents are, the greater the probability of observing the particle as a mixed particle. Under average conditions middling particles are from one-quarter to one-half again as frequent as they appear in polished briquettes.

In respect to mineral composition, polished briquettes are more accurate than in respect to texture. However, a systematic error may result from the fact that all particle sections are assumed to be of the same size (differences in specific gravity being allowed for, if elutriated products are considered) if particles of the type of a shell of one species surrounding a kernel of another are common. This systematic error is to magnify the occurrence of the shell mineral. Generally speaking the error is not large, but it may be significant in special cases.

**Sampling Sized Products for Briquette or Slide Mounting.**—It is well known that fine, closely sized particles of different specific gravities segregate on handling. A small riffing apparatus can be used to advantage to cut the sample to the quantity of material required for the briquette or for the slide. Such a riffing apparatus can be made of brass dividers  $\frac{5}{1000}$  in. thick and of brass stock sheet,  $\frac{1}{8}$  in. thick. The apparatus is about  $1\frac{1}{2}$  in. long, 2 in. broad, and  $2\frac{1}{2}$  in. high; with it can be used  $1\frac{1}{8}$ -in. square receiving pans and a rectangular, flat-bottomed feeding scoop 1 in. long and  $\frac{3}{4}$  in. deep, milled from  $\frac{1}{8}$ -in. brass stock sheet.



**CHEMICAL EQUIPMENT AND LABORATORY**

The chemical equipment required consists largely of the equipment necessary for analytical work, that is, work benches, scales, balances, hot plates, filters and filter racks, burettes for dispensing reagents, pipettes, titrating burettes, beakers and other glassware, muffle and assay furnaces, a drying oven, and a distilled-water still.

Considerable trouble was experienced in several flotation laboratories using distilled water because copper tanks were used to store the distilled water. On account of their great effect in many flotation circuits, copper salts should be positively eliminated from the water; oxidation and carbonation of copper which is corroded, even by partly aerated distilled water, preclude the use of copper tanks unless they are properly tinned: glass storage tanks are best suited for distilled-water storage.

In flotation laboratories where research problems are carried out it is desirable to have, besides the equipment for routine analytical equipment, suitable apparatus for refined chemical analyses of substances in very small quantities, for water analyses<sup>(32)</sup>, and for organic chemical syntheses.

One of the most convenient methods for the analysis of very small quantities of reagents is color matching. This is best done in an apparatus known as a colorimeter. A number of colorimeters have been placed on the market; they are based on the principle of bringing into juxtaposition, in the field of vision, the light allowed to pass through two vessels containing the unknown and a standard, respectively, and of changing the standard until it just matches the unknown.

The equipment required for organic synthesis and analysis is of a rather special nature; the reader is therefore referred to the standard works<sup>(1)(9)(20)(35)(37)(39)(51)</sup>. For inorganic analytical methods the reader is again referred to the standard works<sup>(2)(24)(32)</sup>.

**CRUSHING, GRINDING, AND SIZING EQUIPMENT AND TESTING**

**Grinding.**—The equipment required for the dry crushing of samples includes sample splitters, a small jaw crusher, crushing rolls, a disk pulverizer, and a set of coarse screens. For wet grinding a small pebble mill made of porcelain is most convenient. A small ball mill made of steel pipe and using steel or cast-iron balls is also desirable.

A convenient mill has been designed by the staff of the United Verde Copper Company. It consists essentially of a cylindrical pipe section to which a bottom cap has been welded and on which a top cap can be clamped. Welded upon the cylindrical part of the mill are two prongs for lifting by a small block-and-tackle or by hand. Where infrequent use of a metal mill is expected, it is sufficient to secure a piece of 10-in. pipe threaded at both ends and to use prong-fitted caps for the two ends. The prongs are for the purpose of giving the operator a hold on the mill when opening it. The disadvantage of this type of mill as compared with the United Verde type is in the lodging of ground ore in the threads between the pipe and the caps, which makes it occasionally difficult to open.

A coarse screen should be provided for receiving the ball mill discharge, and can either be mounted on the mill itself or else be placed over a pan. This is for the purpose of separating the grinding medium from the ore.

In practice, greater fineness of grinding is obtained through a reduction in the tonnage fed to each mill, or through increased classifier capacity. In the batch stage of flotation testing, increased fineness is obtained through an increase in grinding time. In general, batch mills are loaded so as to reduce the ore to the desired fineness in 15 to 40 min. A reduction in the time of grinding is, of course, a desirable feature in that it cuts down waiting time; on the other hand, it is inadvisable to design the grinding mill so as to make the grinding time very much shorter than is customary in practice. This is because in practice the ore is conditioned with some reagents while being ground so that a material reduction in the test-grinding time would result; also, in a reduction of the conditioning time. This would cause additional discrepancies between testing and practice.

Buckets and pans are necessary for temporarily storing material during the testing operations; they should preferably be made of white enamel-ware as containers of that type are easy to keep clean, thus minimizing the possibility of loss of ore or of contamination by foreign substances.

**Screening.**—Test screens are required in all sizing operations, the apertures of consecutive screens being in constant ratio. A mechanical shaker is convenient. In a thoroughgoing investigation on the subject, it was found by Hersam<sup>(13)</sup> and by Gross<sup>(14)</sup> that test screening by mechanical means is not so accurate as

test screening by hand. This view, however, does not seem to be shared by all investigators. It may be that a particularly careful worker can obtain more consistent duplication of his own data by hand screening than he can obtain with a mechanical shaker, but this would appear to be untrue of the average operator. Furthermore, the use of a testing-screen shaker eliminates the personal equation and is an enormous time saver. It should therefore be adopted if test work of any magnitude is contemplated.

In view of the fact that over one-half of the feed to flotation is finer than 200 mesh, and that the same is true to an even greater extent of flotation concentrates, it is desirable to adopt an elutriator for the finer sizing operations. Although 400-mesh screens are manufactured, they are delicate and shortly become injured in hands other than those of an expert; also, fine screening is very slow, the screens are expensive, and little would be gained by screening flotation products on a 400-mesh sieve which would retain but a small fraction of the -200-mesh material.

**Microscope Sizing.**—Fine sizing of flotation pulps is obtained by elutriation or by direct measurement under the microscope<sup>(13)(44)(49)(53)</sup>. Except for some very special work, sizing by elutriation should be preferred for the reason that it yields products which can be assayed or otherwise studied, whereas the microscope yields simply some figures. Also, microscope sizing requires all the attention of the operator, but elutriation does not: thus, the elutriation of four samples does not require a fourfold outlay of time if compared with the elutriation of a single sample, but microscope sizing of four samples requires proportionally more time than that of one sample.

The majority of investigators who have carried out microscope sizing tests feel that they are best conducted on sized feeds. This multiplies considerably the number of slides to be prepared and the time required for the sizing operation.

**Principles of Elutriation.**—Elutriation is a sizing operation that depends on the fact that particles of different sizes settle in fluid media at different velocities. The velocity with which a particle settles in a fluid of lesser specific gravity, or rises in a fluid of higher specific gravity is given by Stokes (the law of settling by viscous resistance) as

$$V = \frac{2}{9} a^2 g \frac{(D - d)}{\mu},$$

in which  $a$  is the diameter of the particle,  $g$  the attraction of gravity (substantially constant),  $D$  the density of the particle,  $d$  the density of the medium, and  $\mu$  the viscosity of the medium.

Attention should be called to the fact that this relation does not apply if the particles are too large, and in this connection it is interesting to refer to a diagram by Richards<sup>(40)</sup> in which it is shown that particles settle according to the law of viscous resistance (Stokes) if finer than 0.10 mm. (galena) to 0.14 mm. (quartz): it follows that substantially all flotation products can be elutriated on the basis of Stokes' relation. Stokes' relation was derived for spheres; for irregularly shaped particles whose configuration is not a function of size<sup>(10)</sup>, the factor  $\frac{2}{9}$  should be replaced by a different constant,  $K$ . More generally, then,

$$V = Ka^2g \left( \frac{D - d}{\mu} \right).$$

In general the settling fluid is water, although there is no reason for not using other media, except that they are more expensive. For the elutriation of sulfides, acetone is desirable<sup>(12)</sup>.

The settling velocity depends upon the apparent density; hence particles of the same settling velocity but of different specific gravity have different sizes, the densest being smallest. The difference in the size of mineral particles of different composition but of the same settling velocity may be considered as an objection; with flotation products, however, it is rather an advantage because grinding is nearly always conducted in closed circuit with a classifier, so that the flotation feed is a classified and not a screen-sized product; analysis of such a product with a classifier (an elutriator) rather than with screens is therefore more significant.

**Elutriators.**—Elutriation methods can be classified into those in which the fluid medium is at rest and those in which it is ascending. The method in which the fluid is at rest, or decantation method<sup>(11)(21)</sup>, is more primitive, but gives good results if applied with care<sup>(12)</sup>.

The elutriation method in which the fluid medium is in motion is carried out in a free-settling classifier similar to that described by Richards<sup>(41)</sup> except that it is designed to be run with much slower fluid currents. Many variants of the ascending-current elutriator in which the elutriator tank is of the conical or the cylindrical shape have been proposed. One recent type is shown in Fig. 140. It consists essentially of a long cylindrical glass

tube *A* in which a slow current of water is ascending. The bottom of the tube is fitted with a filtering funnel *C*. Water for the rising current is fed from a constant-head tank through a three-hole feeding bottle *D* to the bottom of the elutriating column. The volume of water fed per unit time is regulated by means of a pinchcock *F* placed on the rubber tube leading from the constant-head tank to the three-hole feeding bottle. By first adjusting the current in the elutriator to a small value, the very fine particles are removed; this is followed by greater and greater fluid speeds to yield coarser and coarser particles in the overflow.

**Operation of Elutriators.**—Considerable attention should be given to proper pulp dispersion in order to obtain significant results. Suspended particles often present a marked tendency to flocculate; this is highly detrimental to elutriation because the clumps of particles behave as though they were a single coarse particle. To disperse pulps a 0.1 per cent aqueous gum arabic<sup>(15)</sup> or sodium silicate<sup>(12)</sup> solution is satisfactory.

#### FLOTATION EQUIPMENT AND ITS USE

The equipment directly used in batch tests consists of hydrogen-ion measuring apparatus, flotation cells, conditioning tanks, reagent pipettes, a water still, distilled-water jars arranged for gravity flow into the flotation cells, reagent-solution jars arranged for gravity flow into measuring cylinders, vanning plaques for the examination of flotation products, filters for dewatering samples, hot plates, scales, and balances.

**Hydrogen-ion Determinations.**—The desirability of determining the hydrogen-ion concentration of flotation pulps has been repeatedly emphasized. The pH should be determined on the tailing water for each flotation test; in those cases in which more than one concentrate is made, the pH should be determined on each concentrate but the last and on the final tailing. Although the pH of the last concentrate water may differ slightly from that of the tailing water, the difference is slight.

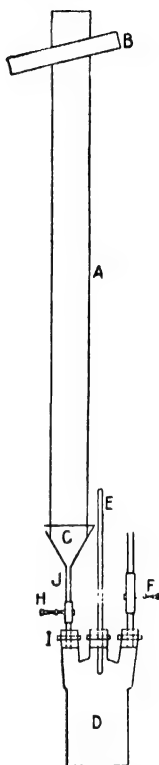


FIG. 140. Elutriator. Cross section.

Diagrams correlating reagent addition with pH (Fig. 141) are valuable in directing the investigator to use the proper amount of pH-modifying reagents; they also serve as qualitative indicators of the soluble-salt content of the ore. Figure 141 was drawn from data obtained with a copper-lead-silver-zinc ore from the Park City District, Utah. Five hundred grams of crushed ore was ground for 15 min. in a porcelain pebble mill, with 500 g. of

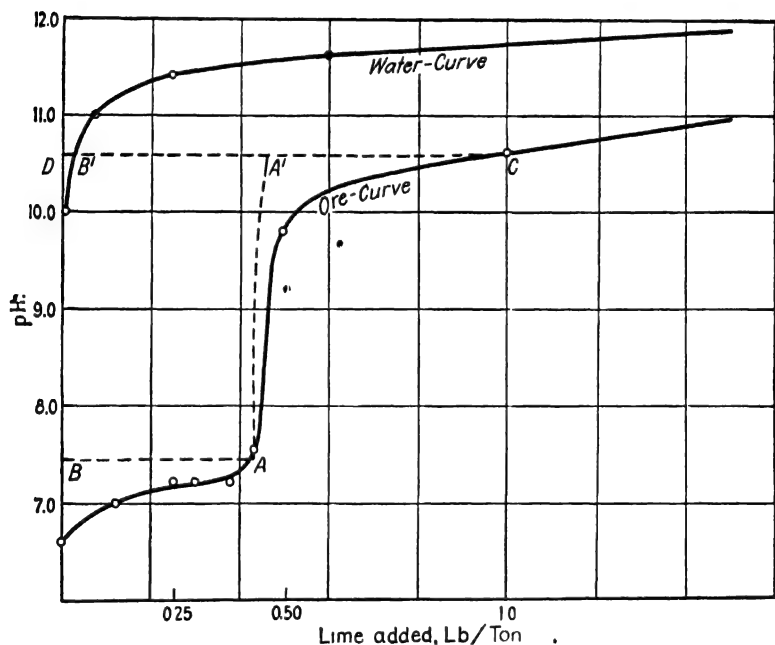


FIG. 141.—Correlation of reagent addition to pH.

distilled water having a pH of 6.0, and varying amounts of lime. After grinding, the pulp was filtered, rejecting the first portion of the filtrate whose pH might have been changed by the filter paper, and the pH of the remaining filtrate was determined by the colorimetric method. By referring to the "ore curve" the sharp break at A is apparent, as well as the fact that the addition of small amounts of lime has hardly any effect on the pH, contrary to what happens with pure water; it is also clear that after the apparent "buffer" action of the ore has been overcome, the pH of the pulp changes very rapidly with increase in lime addition. The discrepancy between the curve obtained with the ore and

that obtained without the ore can be explained by assuming that the apparent abstraction of lime is due to two causes: (a) abstraction by reaction with soluble salts to an extent equal to the difference in concentrations of the added lime at points *A* and *B*, and (b) removal of the remainder of the abstracted amount by reaction with the mineral surfaces. Thus, with 1.0 lb. of lime, the amount *A'B'* (0.43 lb. per ton) is taken up by reaction with the soluble salts; the amount *A'C* (0.54 lb. per ton), by reaction with the mineral surfaces; and the amount *DB'* (0.03 lb. per ton) is free lime, that is, lime capable of affecting the pH.

**Electrometric Method of Measuring pH.**—There are two general methods for determining the hydrogen-ion concentration of solutions<sup>(3)</sup>. The electrometric method depends upon the fact that solutions having a different hydrogen-ion concentration are at a different potential with respect to a cell of known hydrogen-ion concentration. This is a special case of the fact that a metal is at a different potential from a solution containing ions of the same metal, and that the difference in potential between the metal and the solution depends upon the concentration of the metal ions in solution. It follows that a difference in potential should exist between two solutions containing a metallic ion at different concentrations; this potential difference can be made apparent by connecting the solutions by a "salt bridge," on the one hand, and by a wire having electrodes of the same metal as is found in the solutions, on the other.

The hydrogen electrode consists of finely dispersed gaseous hydrogen occluded in platinum black mounted on a strip of platinum<sup>(3)</sup>. The platinum of the hydrogen electrode acts simply as a convenient carrier for the gas.

Other electrodes than the hydrogen electrode, notably the calomel electrode, and the recently introduced quinhydrone electrode have gained much favor, because of their greater ruggedness. In practice, the use of two hydrogen electrodes has been given up, one electrode being almost always a calomel electrode whose potential toward a hydrogen electrode is known, and the other a hydrogen or a quinhydrone electrode. An important objection to the hydrogen electrode is that it is difficult to handle. This explains, in part, the success of the quinhydrone electrode. The latter, unfortunately, is not well suited for flotation work because it cannot be used to determine the pH of a solution more alkaline than pH 9.0.

**Colorimetric Method.**—The colorimetric method of determining hydrogen-ion concentration depends upon the fact that certain organic substances ionize differently at different hydrogen-ion concentrations, and that the different ions to which they give rise are of different colors. Thus, phenol red (phenolsulfone-phthalein) is yellow if the hydrogen-ion concentration is higher than  $10^{-6.8}$ , and red if it is lower than  $10^{-8.5}$ ; it changes gradually from yellow to red at intermediate concentrations. Phenol red can be used as an indicator between pH 6.8 and pH 8.5, but it cannot be used at a pH lower than 6.8 or higher than 8.5.

A pH observation at or near the end of the range of one indicator should be considered insufficient, and a further observation should be made with the next lower or higher indicator. The necessity of this added observation has not always been appreciated, and has resulted in costly errors. Thus, in a certain mill using an alkaline circuit the duty of determining the hydrogen-ion concentration was detailed to an incompetent attendant; lime in amounts up to 10 lb. per ton of ore was being added and the metallurgical results were poor. At the same time, the pH was recorded as insufficiently high, and more lime was added. The whole trouble originated in the attendant's ignorance of the necessity of using an additional indicator when the observation turned out to be at the end of a certain indicator's range: he persisted in using nothing but phenol red, recording the pH as 8.4, whereas it was, in reality, in the vicinity of 12. The simple use of the next higher indicator, thymol blue, would have disclosed that the pH was 9.6 or higher, and so on, until a correct observation was obtained.

To make an accurate comparison, the amount of indicator solution should be kept in proportion to the amount of solution to be tested; better still, a constant volume of unknown and a constant amount of indicator solution should be added to each other in a standard container such as a standard test tube and be matched against known standards placed in similar test tubes.

Colorimetric pH determination is made with convenient refinement in the LaMotte hydrogen-ion Roulette Comparator (Fig. 142). The Roulette is suitable for the determination of pH over quite a range due to the fact that it is built to hold three dozen standard test tubes. It consists essentially of a circular frame mounted on ball bearings and holding the standards, which can be rotated in back of the test tubes containing the unknown;



at its center is a 40- or 50-watt lamp. Comparison between the unknown and the standards is made through a slab of frosted blue glass, looking toward the lamp. On the rotating frame are placed, alternately, standard ampoules containing indicators at various hydrogen-ion concentrations and ampoules of distilled water. Three test tubes filled with the unknown solution are placed in front of the revolving frame, the center test tube containing in addition the proper quantity of indicator. By revolv-

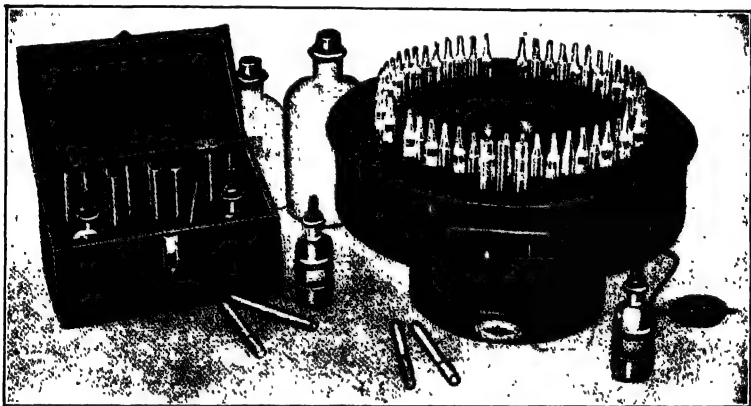


FIG. 142.—Roulette comparator for colorimetric determination of the hydrogen-ion concentration. (LaMotte Chemical Co.)

ing the frame holding the standard ampoules it is possible to find a place for the unknown between two consecutive standards. The object in using three test tubes filled with unknown is to compensate for turbidity.

In the absence of ampoules of standard solutions, the color of the indicator-bearing unknown can be matched with that of standards in color charts<sup>(3)</sup>; this method has been found less desirable because it involves the comparison of a transparent, colored solution with that of an opaque color painted on paper.

Recently a colorimetric method for determining pH in which colored non-fading glass slabs are used in place of standard ampoules containing the indicator solution has been introduced (Hellige pH Comparator). It is said to be highly satisfactory.

**Electrometric vs. Colorimetric Method.**—When compared to the colorimetric method, the electrometric method has some advantages, but many disadvantages. The electrometric method is more accurate, it is not affected by turbidity and is less

subject to "salt effect"<sup>(3)</sup>. On the other hand, it requires considerably more time for each observation, it is more likely to be in error due to careless handling or recording of the readings, and it demands a much higher standard of competence on the part of the operator. Finally, the electrodes are easily poisoned by many substances which chance to be frequently encountered in flotation pulps. Up to the present time there has therefore been little use in flotation for the electrometric method of determining pH.

**Alkalinity Determination by Titration.**—Alkalinity or acidity of mill solutions can be determined by titration with a standard acid or base, using a standard indicator to determine the end point. Phenolphthalein or methyl orange is generally used as indicator but bromthymol blue is somewhat more accurate as it changes color in the pH range 6.5 to 7.5 instead of on the alkaline side as phenolphthalein or the acid as methyl orange.

Titrated alkalinities or acidities of unbuffered solutions can be correlated with pH values by a very simple calculation. Thus, if a solution is found to contain 0.056 lb. free lime per ton of water (equivalent to 0.028 g. per liter), the pH is

$$14.0 - \log_{10} \left( \frac{\frac{1}{2} \times 56.0}{0.028} \right).$$

In buffered solutions, the pH is nearer neutrality than is indicated by a calculation such as the above. Maximum effect of buffering can be estimated from the total  $\text{Ca}^{++}$  concentration. Thus, if 6 lb. lime per ton of ore had yielded a titration of 0.056 lb. free lime per ton of water, after use in a 4:1 pulp, the total  $\text{Ca}^{++}$  is that corresponding to

$$\frac{6}{4} \times 100\%_{2000} = 0.75 \text{ g. CaO}$$

per liter of water. This amount is  $0.75/0.028 = 27$  times the amount of free lime. From the dissociation constant for hydrated lime,

$$[\text{Ca}^{++}][\text{OH}^-]^2 = K,$$

it appears that the maximum buffering action of the  $\text{Ca}^{++}$  not derived from free  $\text{Ca}(\text{OH})_2$  is to reduce the  $[\text{OH}^-]$  to  $1/\sqrt{27}$  of the concentration it would otherwise have. The pH is therefore shifted toward neutrality by an amount not exceeding 0.72.

**Measurement of Pulp Conductivity.**—Conductivity-measuring devices are sometimes used in flotation testing. Inasmuch as they are frequently confused with electrometric (potentiometric)

pH-measuring devices, it is necessary to state that they cannot be used to determine the concentration of the hydrogen ion, but that they measure the total ion concentration, more directly the total current-carrying ability of the solution. Thus a  $10^{-4}$  normal aqueous hydrochloric-acid solution and a  $10^{-4}$  normal aqueous sodium-hydroxide solution conduct approximately the same current, hence the measurement with a conductivity cell is the same; the hydrogen-ion concentration, on the other hand, is very different, the pH being 4 and 10, respectively. Comparison of the hydrogen-ion concentration and of the conductivity, particularly in solutions near the neutral point, can be used as a rough measure of the concentration of the other ions occurring in the pulp besides hydrogen and hydroxyl ions.

Conductivity measurements are obtained through determination of the resistance of a column of electrolyte of known length. This resistance can be measured by the alternating-current Wheatstone-bridge method employed by Kohlrausch, the point of zero current flowing through the bridge being detected by ear phones<sup>(5)(27)(28)(30)(47)</sup>. The circuit employed in conductivity measurements (Fig. 143) is divided into two branches, one of which goes to a wire with a sliding contact *A*, which provides a variable ratio of resistances between *A* and *B* on the one hand, and *A* and *C* on the other; the other branch goes through a conductivity cell *D* and through a resistance *R*. The sliding contact *A* is connected to a point *E* between the cell and the resistance *R*. By moving the sliding contact, the exact position of *A*, when no current is flowing in wire *AE*, is detected by means of the ear phones *P*. When this occurs, the potential at *A* and *E* is the same; hence, the resistance *X* of the cell is

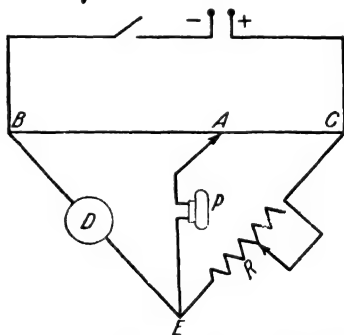


FIG. 143.—Diagrammatic "hook-up" for conductivity measurements.

$$X = r \frac{m}{l - m}$$

if *r* is the resistance of *R* and *m* is the fraction *l* of *BC* represented by *AB*.

**Laboratory Flotation Cells.**—Laboratory flotation cells are of three general types: (a) mechanically agitated, (b) sub-aeration, and (c) pneumatic. For batch testing, sub-aeration machines are preferable.

Most of the test machines of the mechanically agitated type are variants of the pioneer M. S. cell<sup>(19)(45)</sup>. The best known agitation machines are the Janney cell and the University of Utah cell<sup>(25)</sup> (Fig. 144).

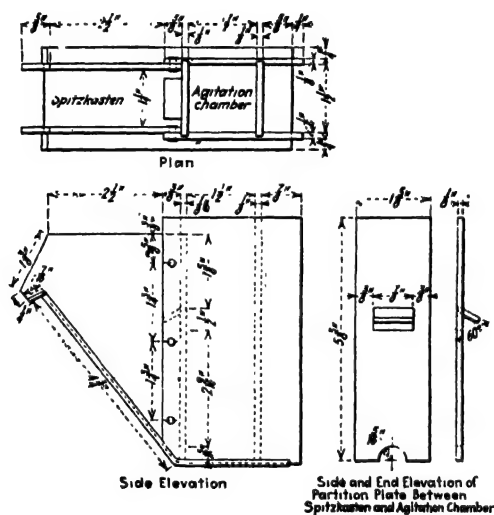


FIG. 144.—Improved University of Utah celluloid testing flotation cell.

The Janney machine is generally built to hold 500 g. of ore per charge and has been extensively used in the past, although favor has shifted in recent years to the machines of the sub-aeration type which feature air control.

The University of Utah machine is remarkable for its small size, the capacity being 50 g. of ore. In design it does not differ materially from the Janney cell, except that the proportions of the agitating compartment and the spitzkasten are different to allow for changes in cross-section and volume of the two chambers. This machine was first designed<sup>(22)</sup> to meet the necessity of determining the floatabilities of small amounts of pure minerals, but its use has been extended to that of acting as cleaner or recleaner for the rougher concentrate obtained from larger machines (*e.g.*, 500- or 1000-g. cells).

Of the sub-aeration type cells the Fahrenwald machine has received much justified favor, largely because of the easy control of air (or gas) introduction.

The Kraut testing machine, a miniature of the full-scale machine (Fig. 106), gives excellent results on many ores because of the particularly effective air control and high rotor speed which it features.

In the line of pneumatic testing machines, the Callow, MacIntosh, and Forrester cells should be mentioned. These machines are very similar to the corresponding large-scale machines, except that they are proportionally narrower. Instead of requiring simply a motor, as the agitation-type machines do, these cells require a motor-fan couple or a compressed-air line.

Careful selection of the structural material for flotation testing cells is more important than for large-scale cells because testing cells have more surface in proportion to their capacity. Indeed, they have approximately as much more surface as their linear dimensions are smaller. Thus, the average 500-g. cell has about ten times as much surface as operating-size cells, and the University of Utah cell about 20 or 25 times as much. For this reason, celluloid cells were devised<sup>(25)</sup>, and are made, in 50-, 100-, 500-, and 1000-g. sizes. These machines, if of the mechanical-agitation or sub-aeration type, are agitated by bakelite or bakelite-lined steel agitators; if of the pneumatic type the gas is introduced through a perforated rubber sheet or glass tubing. The advantages of celluloid as cell material are twofold: (a) increased visibility, and (b) decreased chemical reactivity.

**Technique of Using Flotation Cells.**—Flotation manipulation is very simple: all that is required on the part of the operator is to be consistent in raking the froth when using agitation-type machines, and in the air pressure and quantity of air used in pneumatic machines; to be careful in making up and using reagent solutions; and to keep track of the duration of the preagitation and flotation periods, and of the temperature of the pulp. In other words, in what concerns the flotation operation itself, the operator should strive to be as machine-like as possible, so as to eliminate the "personal equation."

At the same time, the operator should keep his eyes open to note the particular idiosyncrasies of the ore that is being tested. In case the ore tested is complex, and that it is contemplated to collect several concentrates, the operator should examine the

froth every minute or so, by washing some of it on a vanning plaque, in order to decide when to discontinue collecting one froth, and when to introduce reagents for the collection of the next product.

The flotation operator should exert the greatest judgment in the office rather than in the laboratory, that is, when it is decided what reagent combinations or grinding conditions will receive a trial.

**Introduction of Reagents.**—In making up reagent solutions it is advisable to standardize the strength of the solutions to a limited number of concentrations such as are equivalent to 0.001, 0.01, 0.10, and 1.0 lb. per ton for each cubic centimeter of the solutions. The experience of a number of years has taught that this method of making up solutions reduces the possibility of making mistakes, both in the preparation of the solutions and in their use. Among other things, it was found that frother solutions should preferably be made up to the strength of 0.001 or 0.01 lb. per ton for a cubic centimeter; collector solutions to the strength of 0.01 or 0.10 lb. per ton for a cubic centimeter; and solutions of inorganic reagents to the strength of 0.10 or 1.0 lb. per ton for a cubic centimeter, depending upon the general reactivity of the substances and upon the use to which they are to be placed. Although it is preferable to add all substances in solution, because their addition in this way is quicker and more accurate than the addition of solids or oils, it is frequently necessary to use substances like pine oils or thiocarbanilid which are not sufficiently soluble in water, at the concentration at which it is desired to introduce them, for the preparation of solutions. Emulsions of the substances, made by agitating violently a small amount of the substance in a given volume of water in a small graduated cylinder, or alcoholic solutions, in which the alcohol acts simply as a convenient carrier (and somewhat as a frother), can be used.

**Conditioning Tanks.**—It is sometimes desirable to allow the ore pulp to be in contact with reagents for a substantial length of time. This can, of course, be done right in the flotation machine or in conditioning tanks. Large beakers can be used as conditioning tanks, the agitation that is required to keep the pulp in suspension being obtained by a glass stirring paddle.

**Surface Tension Measurement.**—If it is desired to include a surface-tension machine in the laboratory equipment, a machine

of the film-rupturing type should be chosen<sup>(3)(38)(46)</sup>. Film-rupturing machines are based on the principle that the force necessary to rupture a film of length  $L$  is  $2LT$ , where  $T$  is the surface tension, the factor 2 being introduced because the film that is ruptured has two faces. The latest and most accurate apparatus is the Chainomatic surface-tension balance (Fig. 145).

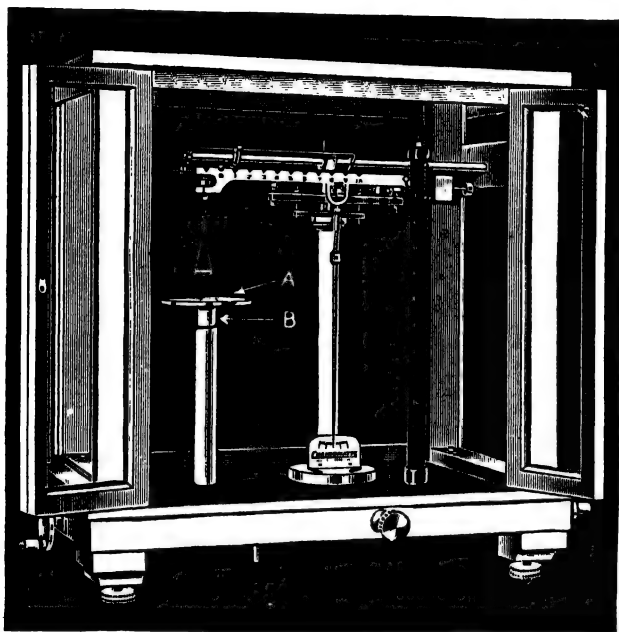


FIG. 145.—Chainomatic surface-tension balance. (Christian Becker Co.)

In using the Chainomatic surface-tension balance a crystallizing dish or watch glass containing the substance whose surface tension is to be measured is placed on the stand which is under the previously cleaned platinum ring; the stand is raised by means of a thumbscrew until the platinum ring touches the surface of the liquid; weights are then moved from notch to notch on the balance beam until the film is ruptured: this yields an approximate value of the load required to rupture the film. The weight on the notched beam is then set to exert a tension that is just smaller than that which would bring about tearing of the film; the stand supporting the crystallizing dish or watch glass is raised to cause contact of the platinum ring with the surface of the liquid, and simultaneous adjustment of the level

of the stand and of the length of the chain weighing on the opposite beam results in tearing the film at such a point that the contact between the ring and liquid surface does not result in any marked pull of the liquid above its normal resting surface. The Chainomatic balance is graduated so as to read in grams the pull required to overcome the surface tension. Knowing the size of the ring, that is the length of the film that is ruptured, and the acceleration of gravity, the value of the surface tension is computed readily.

### ARRANGEMENT OF EQUIPMENT

The equipment that has been described in the foregoing, and the necessary books should be arranged in such a way as to provide ready communication and the least possible interference. This is best done by placing the equipment in a number of inter-connecting rooms. The advantage of such an arrangement will be readily appreciated by any one who has tried to work with a microscope while a sack of ore was being ground in the same room; microscopes are particularly delicate instruments, and should be kept and used away from the polishing apparatus because of the possibility of grit or dust lodging in the instrument and scratching the lenses; the taking of photomicrographs requires an absence of vibration; chemical laboratories are pungent with acid fumes which may affect sacked ores or flotation operations. It is clear that segregation of the various activities is desirable. The various testing operations can be arranged as follows:

*Room 1.*—Office, containing the library and the microscopes. A dark room and a polishing room can be had by suitable partitioning.

*Room 2.*—Chemical laboratory, with balance room set off between the main part of the laboratory and Room 3.

*Room 3.*—Flotation laboratory, arranged with delicate instruments near the balance-room section of the chemical laboratory and the pebble mills at the other end.

*Room 4.*—Cushing and sizing laboratory arranged with the elutriator near the flotation laboratory and the crushing equipment at the other end, properly installed suction fans keeping out the dust. Space should be provided for the reception, cutting, and storing of samples.



A flotation laboratory arranged according to the above outline would be satisfactorily complete. If it is desired to minimize on the installation cost, the least important equipment should be left out, and it might be possible to dispense entirely with some phases of the work. For instance, the chemical laboratory, electrometric hydrogen-ion recorder, pneumatic flotation machines, and the photomicrographic equipment could be left out.

#### KEEPING RECORDS OF FLOTATION TESTS

The records to be kept of the results obtained in testing an ore should include such administrative data as the date on which the work was done, the name of the experimenter, the name and number of the ore sample tested, and the name of the party that supplied the ore. The technical data should include: records of microscope examination, chemical analysis of the ore, crushing and grinding data disclosing the fineness to which the ore was ground, and whether such grinding was wet or dry, and flotation data. The flotation data should include a record of the quantities of reagents added, the place and time of addition of the same, metallurgical results obtained, microscope observations on flotation products, pH records, remarks on the character of the froth, on the flocculation of the pulp, the temperature at which the test was conducted, and the duration of and dilution during preagitation.

Reports should be concisely written and clearly expose the results. Data sheets should be annexed for reference purposes.

## CHAPTER XIX

### METALLURGICAL CALCULATIONS

Flotation results are generally expressed in terms of various numbers. The significance of some of these measures of concentrating operations is easy to grasp. But others are abstract and much usage is required before they become familiar.

**Direct Statement.**—The simplest way to express metallurgical results is by a statement of the weight of the various products derived from a given weight of feed, together with their percentage content of the various metals, minerals, or gangues whose separation is desired. For example, the results of concentrating a copper ore by flotation may be stated as in Table 177.

TABLE 177.—DIRECT PRESENTATION OF FLOTATION RESULTS

Product	Weight, per cent	Metal content, per cent copper	Gangue content, per cent insoluble
Concentrate.....	9.3	18.52	12.6
Tailing.....	90.7	0.15	62.7
Feed.....	(100)	1.86	57.9

Presentation of the results in the form of Table 177, although direct, lacks in interpretative convenience. In order to weigh the advantages of the operation eight numbers are to be kept in mind (five only if the insoluble content is deemed of secondary importance).

**Recovery, Rejection, Losses.**—From the relative weight of the concentrate and tailing and their assays can be figured that fraction of a certain metal or gangue contained in the feed which is recovered in the concentrate. This fraction, when expressed as a percentage, is known as *recovery*. Thus, in the above case, the copper recovery in the concentrate is 92.7 per cent and the insoluble recovery is 2.0 per cent.

By an extension of the definition, the percentage loss of metal in a discarded product, or rejection of gangue, may be regarded as a recovery. At any rate such losses and rejections are mathematically symmetrical to recovery in the concentrate. In the instance of Table 177 the copper recovery in the tailing (copper loss) is 7.3 per cent and the insoluble recovery in the tailing (insoluble rejection) is 98.0 per cent.

**Ratio of Concentration.**—The relative weight of feed to that of concentrate is a measure of the concentration in weight that has been effected. This ratio is known as the *ratio of concentration*.

**Calculation of Recovery.**—The simplest method of calculating recovery involves a knowledge of the weight of each product and its assay.

Let  $A$  be the weight of the first product and  $a$  its assay,  $B$  and  $b$  the corresponding quantities for the second product, and  $F$  and  $f$  the corresponding quantities for the feed.  $Aa$ ,  $Bb$ , . . .  $Mm$ , . . .  $Nn$ , are the amounts of metal in the various products and  $Ff$  that in the feed. Clearly:

$$Ff = Aa + Bb + \dots + Mm + \dots + Nn. \quad (1)$$

By definition, the recovery in the various products is

$$R_m = \frac{Mm}{Ff}. \quad (2)$$

Specifically, for instance, the recovery in the concentrate of an operation making only one concentrate and one tailing is

$$R = \frac{Aa}{Aa + Bb} = \frac{Aa}{Ff}. \quad (3)$$

Recovery may be calculated from the metal contained in the feed  $Ff$  or from that contained in the products,  $Aa + Bb$ . Theoretically the two methods should give the same answer (Eq. [1]); practically they do not. The discrepancy arises from the approximate character of analytical results, from inaccuracies in weighing, and from sundry operating losses.

For experimental purposes, determination of recovery from the products is more accurate. In practice, however, weights of products are generally inaccurately known, so that determination of recovery by exclusion of weights is preferable. In the case of an operation yielding two products only, calculation of recovery by a formula excluding weights (Eq. [5']) is simple enough. If several concentrates are made, the calculation is arduous and

small analytical errors become so magnified in the calculation as to often yield negative answers for some of the smaller recoveries.

In determining recovery without the use of the weights  $A, B, C$ , use is made of identity (4):

$$F = A + B + \dots + M \dots + N. \quad (4)$$

Equation (4) together with  $n$  equations similar to Eq. (1) allows an elimination of  $A, B, \dots, M, \dots, N$ .

In the case of operations involving the production of one concentrate ( $C, c$ ) and one tailing ( $T, t$ ) only, the equations are:

$$\begin{cases} Ff = Cc + Tt, \\ F = C + T; \end{cases}$$

putting  $F = 1$  (which is permissible),

$$C = 1 - T,$$

hence,

$$\begin{aligned} f &= (1 - T)c + Tt, \\ &= c - T(c - t), \end{aligned}$$

or

$$T = \frac{c - f}{c - t}; \quad C = \frac{f - t}{c - t}.$$

Substituting these values in Eq. (3):

$$R_c = \frac{f - t}{c - t} \cdot \frac{c}{f}; \quad R_t = \frac{c - f}{c - t} \cdot \frac{t}{f}. \quad (5)$$

Expressing recoveries on a percentage basis:

$$R_c = \frac{f - t}{c - t} \cdot \frac{c}{f} \cdot 100; \quad R_t = \frac{c - f}{c - t} \cdot \frac{t}{f} \cdot 100. \quad (5')$$

**Calculation of Ratio of Concentration.**—Ratio of concentration is defined as the ratio of the weight of feed to that of concentrate. It is therefore  $F/C$ . But since

$$C = \frac{f - t}{c - t} \text{ and } F = 1,$$

the ratio of concentration  $K$  becomes:

$$K = \frac{c - t}{f - t}. \quad (6)$$

**Usefulness and Limitations of Recovery, Rejection, and Ratio of Concentration.**—Metal recovery, gangue rejection, and ratio of concentration describe a concentrating operation less directly than actual weights and assays, but by the use of three numbers instead of five (or eight).

Metal recovery (in concentrate) has a direct practical significance, as it is that percentage of the total metal in the ore which is actually available for further processing.

Ratio of concentration, also, has a practical significance in that it is a rough measure of the freight and smelting economies resulting from concentration. Thus, if a ratio of concentration of 10 is attainable in place of a former ratio of 5, it is clear that freight charges and smelting costs would be approximately one-tenth instead of one-fifth the charge and costs on the raw ore—one-half as large in the case of the second concentrating operation as in that of the first operation.

Gangue rejection has no direct economic significance, since it is a measure of the rejection of a worthless constituent. Yet if concentration is viewed as strictly a process whereby mixed substances are segregated, it is just as important as metal recovery.

The advent of selective flotation has caused attention again to be focused on this fact since one or more of the minerals are made to play the part of gangue during the flotation of another mineral.

The difficulty of evaluating the relative quality of flotation operations from such series of numbers as metal recovery, gangue rejection, and ratio of concentration has led to a search for single-number criteria of segregation<sup>(1)(2)</sup>.

The *metallurgical efficiency* proposed by R. W. Diamond has many practical applications. In this book *selectivity index*<sup>(3)</sup> has been chosen in preference to other single-number criteria of segregation for the reason that it weighs more adequately the relative merits of crude separation and of refined selection.

**Calculation of Metallurgical Efficiency.**—In an operation involving the production of  $n$  products each of which is a concentrate of some kind (even the tailing which may be regarded as waste concentrate), metallurgical efficiency is the arithmetical mean of the various recoveries in the respective concentrates:

$$E = \frac{\sum_o^n R_{mM}}{n} \quad (7)$$

Specifically if one concentrate and one tailing only are made, and the recovery of metal in the concentrate is  $R_{aA}$  and that of waste in the tailing is  $R_{bB}$ , the metallurgical efficiency is

$$E = \frac{R_{aA} + R_{bB}}{2}$$

Similarly if a lead concentrate, zinc concentrate, iron concentrate, and tailing are made,  $R_{aA}$  being the recovery of lead in the lead concentrate,  $R_{bB}$  that of zinc in the zinc concentrate,  $R_{cC}$  that of iron in the iron concentrate, and  $R_{dD}$  that of non-sulfide gangue in the tailing, the metallurgical efficiency is

$$E = \frac{R_{aA} + R_{bB} + R_{cC} + R_{dD}}{4}$$

**Calculation of Selectivity Index.**—Selectivity index is the geometrical mean of the relative recoveries and relative rejections of two minerals, metals, or groups of minerals or metals.

If  $R_a$  is the recovery of  $a$  in  $A$  and  $J_a$  is the rejection of  $a$  in  $B$ , and  $R_b$  the recovery of  $b$  in  $A$  and  $J_b$  its rejection in  $B$ , the relative recovery of  $a$  to  $b$  is  $R_a/R_b$ , and the relative rejection of  $b$  to  $a$  is  $J_b/J_a$ . Hence:

$$\text{S.I.} = \sqrt{\frac{R_a}{R_b} \cdot \frac{J_b}{J_a}} \quad (8)$$

But

$$J_a = 100 - R_a; \quad R_b = 100 - J_b$$

Hence:

$$\text{S.I.} = \sqrt{\frac{R_a \cdot J_b}{(100 - R_a)(100 - J_b)}} \quad (9)$$

For example, if lead recovery in a lead concentrate is 95 per cent and gangue rejection in delead pulp is 96 per cent,

$$\text{S.I.} = \sqrt{\frac{95 \times 96}{5 \times 4}} = 21.3.$$

In some cases it is easier to determine selectivity indices from grades than from recoveries. Thus if assays for substances  $a$  and  $b$  are  $M$  and  $N$  in the concentrate and  $m$  and  $n$  in the tailing, it can be shown that the selectivity index is

$$\sqrt{\frac{M}{m} \cdot \frac{n}{N}}$$

In the case of Table 177, for instance, the selectivity index is

$$\text{S.I.} = \sqrt{\frac{18.5}{0.15} \times \frac{62.7}{12.6}}$$

**Use of Selectivity Index.**—Substitution of a selectivity index for mineral recovery, ratio of concentration, and gangue rejection permits the quantification of the selection under consideration by one number only, and thus the making of all sorts of comparisons which would otherwise be difficult or impossible.

TABLE 178.—RELATION OF SELECTIVITY INDEX TO OTHER MEASURES OF THE EFFECTIVENESS OF CONCENTRATING OPERATIONS

Selectivity index	Metal recovery	Gangue rejection	Metallurgical efficiency
2	50	80	65
	60	73	66.5
	70	63	66.5
	80	50	65
	90	31	60.5
3	60	86	73
	70	79	74.5
	80	69	74.5
	90	50	70
5	60	94	77
	70	91.5	80.7
	80	86	83
	90	73.5	81.7
	95	57	76
7	80	94	87
	90	88	89
	95	77	86
10	80	96	88
	90	92	91
	92	90	91
	95	84	89.5
15	90	96.2	93.1
	92	95.2	93.6
	94	93.5	93.8
	96	90.4	93.2
25	90	98.6	94.3
	92	98.2	95.1
	94	97.5	95.8
	96	96.3	96.1
	98	92.9	95.5
50	96	99.1	97.6
	97	98.7	97.8
	98	98.2	98.1
	99	96.2	97.6
100	97	99.7	98.3
	98	99.5	98.8
	99	99.1	99.0
	99.5	98.2	98.9

In view of the practical importance of mineral recovery and of its universal use, metallurgical results are stated in this book in terms of both recovery and selectivity index.

**Comparison of Selectivity Index to Other Measures of Concentration.**—Table 178 correlates various selectivity indices with recoveries, and metallurgical efficiencies.

**Economic Recovery.**—From an economic standpoint neither recoveries nor ratios of concentration nor selectivity indices afford a comprehensive appreciation of the economic effectiveness of a concentrating operation. It has been proposed<sup>(4)</sup> to use to this effect a new quantity called *economic recovery*. This is the percentage ratio of the actual value of the concentrate obtained per ton of ore to the value of that weight of concentrate theoretically obtainable in mineralogically pure form from a ton of ore.

Economic recovery may be illustrated by the following example: 0.15 ton of lead concentrate worth \$50.00 per ton can be realized in practice from an ore which theoretically should yield 0.14 ton of mineralogically pure lead (galena) concentrate worth \$75.00 per ton. Even though the actual lead recovery may be as high as 95 per cent, the economic recovery is only

$$\frac{0.15 \times 50}{0.14 \times 75} = 71.4 \text{ per cent.}$$

At first sight, "economic recovery" appears extremely attractive. However, it is open to several objections, some of which are technical and others economic. The principal objections are the following:

1. Since ores are variable (even those treated at any one mill) and frequently contain more than one valuable mineral, the composition of the mineralogically pure concentrate will vary from day to day.
2. The value of the mineralogically pure concentrate will vary from day to day, even though it were to have a uniform composition, because of fluctuations in metal prices. This is partly, but not wholly, compensated by variations in the value of the actual concentrates.

**Graphical Presentation<sup>(5)(6)</sup>.**—Every year the Cartesian method of presenting data by means of rectangular coordinates has been winning more favor. In comparison, tabular presentation is clumsy and requires more effort on the part of the person who is to assimilate the information.



Yet, in spite of the recognition that has been earned by the graphical presentation of data, full advantage is taken of that method by a small percentage of its users. Thus it is only occasionally recognized that other scales of coordinates than the arithmetic scale have merit.

The logarithmic scale of coordinates is of very great usefulness for the presentation of certain data. Its usefulness lies in that different values of the same variable are visualized in the term of their ratio rather than in the term of their difference (as they would if the customary arithmetic scale were used).

The principal independent variables encountered in flotation work are (1) reagent addition, (2) time, (3) temperature, (4) pH, (5) particle size. The principal dependent variables are (6) recovery, (7) ratio of concentration, (8) metallurgical efficiency, (9) selectivity index. In presenting the relationship between dependent and independent variables, the latter should preferably be the abscissas.

For time, reagent addition, temperature, recovery, ratio of concentration, and metallurgical efficiency it is best to use an arithmetic scale. For pH, particle size, and selectivity index a logarithmic scale is best. This rule, should, of course, not be considered as hard and fast, but as a broad generalization which is proved by its exceptions.

It is convenient in many instances to use what appears to be an arithmetic scale, but is in reality a logarithmic scale. This is the case, for instance, in dealing with particle size: particles in a ratio of constant size are plotted at equidistant positions along an axis of abscissas. It is also the case in the customary arithmetic pH scale, pH being a logarithmic function of the hydrogen-ion concentration.

The use of logarithmic and arithmetic scales leads to charts of three types. In one both scales are arithmetic, in the second both are logarithmic, and in the third one scale is arithmetic and the other is logarithmic.



## CHAPTER XX

### EFFECT OF FLOTATION ON MINING, METALLURGY, AND METAL MARKETS

In concluding the study which has been presented in this book of the art of flotation, it is fitting to consider the effect that the newcomer has exerted on existing processes, on mining operations, and on the price of metals.

**Ore Dressing.**—The most obvious effect of flotation has been on ore dressing which it has revolutionized. In the course of the past few years, scarcely any gravity concentrating installations have been erected, but many have been torn down to be replaced by flotation plants.

Mill men trained in the older methods have found it difficult to adjust themselves to perceiving the delicate reactions of flotation. From relatively crude mechanical surroundings the mill man has had to familiarize himself with complicated chemical phenomena. Those who have been able to adjust themselves have survived and made satisfactory flotation operators. But, in the main, there has been a large demand for young operators trained in the newer art.

Obsolescence of machinery has been even larger, and with the passing of gravity concentration as the dominant ore-dressing process has gone the multiplicity of belts, launders, and clumsy pulleys of a former day. In comparison, modern flotation plants are a model of neatness, simplicity, and extensive mechanization.

**Hydrometallurgy.**—With the lowering grade and increasing complexity of the ores being mined about 25 years ago, and the impossibility to effect suitable recoveries by gravity concentration, hydrometallurgy loomed as the dominant ore-treatment scheme for low-grade ores. But the development of flotation has arrested the growth of leaching.

In the treatment of copper ores, flotation is more advantageous if the ore is a sulfide, but leaching is at least equally suited if the ore is oxidized. In the treatment of lead ores leaching cannot compete with flotation unless extremely cheap salt and sulfuric



# INDEX

## A

- Adsorption, 17, 22
  - by crystals, 20
  - exchange, 22
  - Gibbs' relation, 17
  - Langmuir, 18, 21
  - nature of, 21
- Airlifts, 405
- Alcohol, amyl, 58
  - heptyl, 58
  - hexyl, 58
- Alkalinity, control, 184
  - determination, 512
  - by titration, 512
- Allen, law of motion, 104
- Alpha-naphthylamine, 74
- Amalgamation, 324
  - vs.* flotation, 478
- Amine, 164
- Amortization, 434
  - magnitude, 436
- Anaconda mill, 182
  - alkalinity control, 184
  - crushing, 134
  - flow-sheet, 134, 183
  - grinding, 134
  - minerals, 181
  - ore, 176, 181
  - particle size, 143, 145
  - reagents, 184
  - results, 184
- Analysis, mineralogical (*see* Mineral-  
ogical analysis)
  - proximate, 120
  - ultimate, 120
- Ångström, 10
- Antitoxic agents, 79
- Apatite concentration, 371
  - magnetite separation, 372
- Argentite, on sphalerite, 130

- Arsenic-antimony separation, 335, 336
- Arsenopyrite, 336
- Atom, 9
  - Bohr model, 10
  - Lewis-Langmuir model, 10
  - nucleus, 10

## B

- Bakelite, for briquettes, 496
- Ball mill, 133, 504
- Barite concentration, 373
- Barrett oil, 229, 232
- Batch testing, 488
- Bauxite flotation, 376, 377
- Blowers, 406
  - Roots, 406
- Bornite, 167, 168
  - chalcocite-sphalerite separation, 272
  - sphalerite separation, 271
- Bournonite, 197
- Briquettes, 496
  - equipment, 496, 497
  - preparation, 496
- Britannia mill, 187
  - costs, 192
  - flow-sheet, 188
  - gold recovery, 189
  - lime requirement, 191
  - ore, 176, 187
  - pyrite recovery, 189
  - reagents, 190
  - results, 190
  - retreatment, 189
- Brownian movement, 40, 45, 151
- Bubble, appearance, 101
  - armored, 94
  - column, 92
  - filter, 116

Bubble, flow-lines around, 91  
 mineralization, 112  
 mineralized, 101  
   ascending velocity, 102  
   minimum size, 106  
   specific gravity, 102  
 overmineralized, 113  
 particle encounter, 88  
   probability of, 90  
 size, 100  
 structure, 100  
 undermineralized, 113  
 Buffer action, 31  
 Bulk-oil flotation, 2, 111

## C

Calcite, activation, 359  
 flotation, 359  
 inhibition, 361  
 mass-action relations, 360  
 pH, 359  
 -quartz separation, 363  
 Calumet and Hecla ore, 176  
 flow-sheet, 193  
 results, 194  
 Camphor oil, 63, 270  
 Cananea, cyanide, 171  
 lime, 170  
 particle size, 143  
 Capacity of plant, 411  
 marketing considerations, 413  
 milling considerations, 411  
 mining considerations, 412  
 most economical, 412  
 transportation considerations, 412  
 Capital costs, 438  
 design, 439  
 erection and installation, 440  
 factors, 438  
 machinery, 440  
 mill building, 439  
 principal items, 439  
 Caprylic acid, 70  
 Carbonates, separation from each  
   other, 366  
 Carborundum, 13  
 Cascade gas introduction, 88

Cassiterite, 377  
 -feldspar separation, 379  
 pH, 378  
 -quartz separation, 378  
 Catalysis, heterogeneous, 21  
 phenyl thiourca, 21  
 Catalyst, 20  
 Cerussite, 76, 77  
 -calcite separation, 296  
 pH, 298  
 sodium sulfide, 77  
 thiocresol, 287  
 xanthates, 298  
 sulfidizing, 294  
 Chalcocite, 164  
 -bornite-sphalerite separation, 272  
 collectors, 164  
 cyanide, 164  
 -galena separation, 277, 278  
   fineness of grinding, 277  
   inhibiting agents, 278, 279  
   pH, 279  
   strong collector, 279  
 inhibitors, 164  
 pH, 163  
 -sphalerite separation, 273  
 Chalcopyrite, 165  
 cyanide, 167  
 -galena separation, 279  
 cyanide, 280  
 particle size, 281  
 practical illustration, 281  
 lime, 167  
 in marmatite, 217  
 -marmatite ores, 250  
   from Amulet mine, 257  
   from Arizona, 266  
   from British Columbia, 253  
   from Manitoba, 256  
   practice, 258  
   from Rouyn, Que., 250  
 oxidizing agents, 167  
 separation from pyrite, 166  
 in sphalerite, 123, 217  
 sulfide ion, 167  
 Changes, in hydrometallurgy, 531  
 in ore dressing, 531  
 in pyrometallurgy, 531

- Chemical analyses, 503
  - equipment, 503
- Chief Consolidated mill, 302
  - flow-sheet, 302
  - reagents, 303
  - results, 303
- Chloritization, 130
- Chromates, 78
- Chromic salts, 79
- Cinnabar flotation, 338
- Circuits, separation of, 425
- Circulating loads, 491, 492
- Classifiers, 134, 139
  - Akins, 410
  - arrangement, 423
  - bowl, 409
  - Dorr, 410
  - hydraulic, 139
  - rake, 139, 409
  - spiral-ribbon, 139, 410
- Classifying, 491
  - modern trends, 137
- Cleaner tailing fluctuations, 426
- Cleansing agents, 77
- Climax mill, 340
  - flow-sheet, 340
  - results, 341
- Coal, 350
  - American results, 354
  - bone, 351
  - calcium sulfate in, 351
  - constitution of, 351
  - English results, 353
  - flotation, economic limitations, 353
  - impurities in, 351
  - inherent ash in, 351
  - oxidation, 352
  - pyrite in, 351
  - reagents, 352
  - specific gravity, 350
  - sulfur in, 351
  - tar, 74
    - creosote, 74
- Collection, by metathesis, 65
  - by surface adsorption, 64
- Collective flotation, 6
  - vs.* selective flotation, 482
  - copper ores, 483
  - lead-zinc ores, 485
- Collector, 55, 63, 64
  - chemicals *vs.* oils, 175
  - molecular structure, 68
  - selective, 68
  - used in practice, 69
- Colloids, definition, 40
  - in flotation, 40
  - lyophilic, 41
  - lyophobic, 41
  - mutual precipitation, 52
  - particle size, 40
  - protective, 41, 75
    - in coal flotation, 352
  - silver iodide, 43
  - stabilization, 42
  - system, 40
  - types, 41
- Comminution, 132
- Concentrate, bins, 443
  - definition, 1
  - optimum grade, 471
- Concentrating action, Callow cell, 93
  - Minerals Separation cell, 95
- Conditioning, 301
  - tanks, 401
  - testing, 516
- Contact angle, 33, 34
- Copper Cliff concentrator, 286
  - flow-sheet, 287
  - pH, 288
  - reagents, 288
- Copper-iron ores, 174
  - lead ores, 248, 273
    - economics of separation, 274
    - mineral associations, 276
  - lead-zinc separation, 284
    - proposed flow-sheet, 284
  - native (*see* Native copper)
  - nickel ores, 248, 284
    - occurrence of nickel, 286
- ores, 156
  - cyanide, 170, 171
  - disseminated, 157
  - flaky silicates, 159
  - gangue elimination, 157
  - lead-bearing, 274
  - massive sulfides, 157
  - minor problems, 159
  - porphyry, 157

- Copper ores, pyrite elimination, 157
    - tonnage, 156
    - types, 157, 158
    - plant design, 428, 429
    - salts, 205, 206, 282
    - smelter schedule, 458
    - sulfate, 5, 76
    - sulfides, 150
      - Cananea, 170, 171
      - chemicals *vs.* oils, 175
      - Eustis, 172
      - iron-bearing, 168
      - lime, 170
      - non-iron bearing, 169
      - reagent consumption, 172, 173
      - Utah Copper recovery, 169
    - value in concentrate, 460
    - zinc ores, 248
      - economic features, 248
      - technical features, 248, 249
  - Corundum, 376
  - Cost, 433
    - average, 455
    - Britannia, 192
    - capital (*see* Capital costs)
    - classification, 433
    - distribution, 454, 455
    - insurance, 437
    - operating (*see* Operating costs)
    - overhead, 433
    - patent royalties, 437
    - personnel, 437
    - taxes, 438
  - Covellite, 167
    - on sphalerite, 206
  - Cresosote, coal-tar, 74, 237
  - wood-tar, 74, 232
  - Cresol, 58, 62
    - surface tension, 59
  - Cresylic acid, 62, 237
  - Crushers, cone, 133
    - gyratory, 133
    - jaw, 133
  - Crushing, 132
    - arrangement, 421
    - coarse, 133
    - intermediate, 133
    - practice, 132
    - stage, 132
  - Crushing, Sullivan plant, 135
  - Crystalloid, 40
  - Cupferron, 378
  - Custom plants, 472
    - design, 472
    - vs.* direct smelting, 475, 476
      - lead ores, 475
      - lead-silver ores, 476
    - ore purchases, 474
    - vs.* small mills, 473, 474
  - Cyanidation, freight charges, 479
    - vs.* flotation, 478-480
      - character of ore, 478
      - treatment cost, 478
    - tailing, flotation of, 330
  - Cyanide, 77, 161, 170, 171, 206, 210
    - chalcocite, 164
    - chalcopyrite, 167
- D
- Deactivating agents, 76
  - Depreciation, 434
  - Depressing agents, 55, 78
  - Dichromate, 6, 203, 204, 210, 268
  - Differential flotation, 6
  - Dilution, 45, 117, 118
  - Dioxyphenylthiourea, 75
  - Dispersion, 43
    - desirable for flotation, 49
    - effect of dilution, 44
    - regulators, 80
  - Distributors, 402
  - Disulfide, organic, 164
  - Dithiocarbamates, 74
  - Dithiophosphates, 74, 169, 180, 229
  - Dixanthogen, 72
  - Dry silver ores, 337
- E
- Economic recovery, 528
  - Electrode, calomel, 509
    - hydrogen, 509
    - quinhydrone, 509
  - Electron, 10
    - shared, 13
    - transferred, 13
    - valence, 11



- Electrostatic effects, 99
  - Elutriation, 505
  - Elutriators, 506
    - operation, 507
  - Enargite, 167, 168
    - galena separation, 283
    - cyanide, 285
    - dichromate, 284
  - Enrichment, secondary, 125-127
    - copper ores, 128
    - Utah Copper ores, 128
  - Eucalyptus oil, 62, 246
  - Eustis Copper, 172
- F
- Fatty acid, 69, 201, 295, 306
    - intermediate, 70
  - Feed-assay fluctuations, 423
  - Feldspar, 32, 381
    - activation, 381
    - garnet separation, 383
    - quartz separation, 382, 383
    - sericite separation, 383
  - Ferberite concentration, 372
  - Ferricyanide, 164
  - Ferrite, 213
  - Ferrocyanide, 164
  - Films, monomolecular, 18, 19
  - Filter, American, 407, 408
    - centrifugal, 408
    - cost, 443
    - Dorrco, 408
    - requirement, 443
  - Filtration, direct without thickening, 428
  - First cost (*see* Capital cost)
  - Flaky silicates, 159
  - Flin Flon mill, 260
    - flow-sheet, 261-263
    - pH, 266
    - pilot-plant, data, 261
    - reagents, 264
    - reagent, consumption, 265
      - discussion, 265
    - talc flotation, 264
  - Floatability, native, 37, 38
  - Flocculation, 43
    - critical size, 47
  - Flocculation, electrolytes, 49, 52
    - and flotation, 49
    - particle collision, 47
      - adhesion, 47
    - pH, 50
    - vs.* sedimentation, 44
    - valence, 51, 52
  - Floor space, 440
    - concentrate disposal, 443
    - filtering, 443
    - flotation, 440
    - thickening, 443
  - Flotation, arrangement, 423
    - bulk oil, 2
    - chemical *vs.* oil, 5
    - colloids, 40
    - vs.* cyanidation (*see* Cyanidation *vs.* flotation)
    - definition, 1
    - vs.* direct smelting, 466
      - copper ores, 467
      - effect of feed grade, 466, 467
      - of freight rates, 472
      - of minor metals, 469, 470
      - lead ores, 468
    - etymology, 1
    - future development, 534
    - vs.* gravity concentration, 481
    - historical survey, 1
    - vs.* leaching, 477
    - phases, 24
    - physico-chemical foundations, 9
    - testing, 488
      - records, 519
    - vs.* Trent process, 357, 358
  - Flotation machines, 387
    - agitation type, 389
    - Callow, 183, 228, 230, 326, 341, 396
      - concentrating action, 93
    - capacities, 390
    - Colburn and Colburn, 390
    - Cole, 400
    - comparison, 400
    - cost, 441
    - Denver Sub-A, 391
    - Eberenz and Brown, 390
    - Elmore, 87, 96
    - Fagergren and Green, 394

- Flotation machines, Forrester, 189, 228, 399
- Groch, 394
- Hebbard, 394
- Hoover, 4, 96
- Hunt, 186, 399
- Inspiration, 398
- Janney, 180, 395
- K. and K., 394
- Kraut, 304, 392
- Lemmon-Hebbard, 325
- MacIntosh, 282, 287, 331, 397, 398
- mat-type, 398
- Mishler, 390
- Minerals Separation, advantages, 391
- concentrating action, 95
- standard, 187, 189, 193, 235, 240, 244, 388
- sub-aeration, 182, 228, 230, 235, 241, 261, 290, 302
- M. K. type, 269
- Myers, 400
- Owen and Dalton, 226
- pneumatic *vs.* agitation, 115
- principles, 388
- requirements, 387
- Ruth, 333, 394
- Southwestern, 398
- advantages, 399
- capacity, 400
- testing (*see* Testing cells)
- Flow-sheet, Anaconda, 183
- Britannia, 188
- Calumet and Hecla, 193
- Chief Consolidated, 302
- Climax, 340
- Copper Cliff, 286
- copper-lead ores, 284
- Flin Flon, 261-263
- Ikuno, 269
- Independence, 332
- lead ore, 224
- Miami, 186
- Midvale, 240, 241
- Morning, 225
- rhodochrosite concentration, 366
- Sherritt-Gordon, 258
- Sullivan, 135, 235, 236
- Flow-sheet, Timber Butte, 229
- Tooele, 244
- Tul-mi-chung, 325
- Utah-Apex, 282
- Utah Copper, 180
- Fluorite, 32, 367
- calcite separation, 368
- quartz separation, 367, 368
- reagents, 368
- Froth, 56, 86
- character, 116
- effect of colloids, 110
- of oil, 111
- of particle size, 110
- operative, 112
- cleaning, 114
- formation, 107
- gummy, 114
- persistence, 113
- polygonal, 108, 109
- production, 56, 86
- water content, 115, 116
- weeping, 56
- Froth-flotation, 2
- Delprat, 3
- Froment, 3
- Potter, 3
- Sulman, Picard and Ballot, 3
- Frother, 54, 56, 62
- molecules, composition, 58
- polar groups, 61, 68
- structure, 58
- in practice, 62
- requirements for, 61, 62
- Frothing and surface tension, 56
- mechanism, 58
- G
- Galena, 198
- barite-silica separation, 374
- chalcocite separation (*see* Chalcocite-galena separation)
- chalcopyrite separation (*see* Chalcopyrite-galena separation)
- collectors, 199, 200
- dichromate, 203
- and xanthate, 204

- Galena, fatty acids, 201
    - inhibiting agents, 202
      - cations, 202
    - oxidation, 198
    - pH, 204
    - soaps, 201
    - toxic action of cations, 203
    - xanthate, 199
      - abstraction, 198, 199
  - Gangue, 120
  - Gas dispersion, method for, 107
  - Gas introduction, 86
    - agitation, 88
    - cascade, 88
    - mechanical generation, 86, 87
    - pneumatic, 88
    - precipitation, 95, 97
    - sub-aeration, 88
    - vacuum generation, 86, 87
  - Gas-solid attachment, agitation machines, 95
    - direct-contact hypothesis, 96
    - effect of polarity, 99
    - electrostatic effects, 99
    - gas-precipitation hypothesis, 95
    - pneumatic machines, 9
    - selection in, 98
    - sub-aeration machines, 98
  - Gasoline, 356
  - Gelatin, 42, 75
  - Gibbs' adsorption theorem, 17
  - Gold-antimony separation, 335, 336
  - Gold, at Britannia, 189
    - copper ores, 322
      - amalgamation preceding flotation, 324
      - collective *vs.* selective flotation, 322
      - flotation followed by cyanidation of tailing, 323
    - mineralogical occurrence, 320
    - native, 324
    - ores, antimonial, 334
      - arsenical, 334
      - carbonaceous, 334
      - principal types, 321
      - summary, 326
      - telluride, 332
  - Gold-pyrite ores, 327
    - fineness of grinding, 330
    - flotation of cyanidation tailing, 330
    - Rand experiments, 331
    - Rand flow-sheet, 332
    - reagents, 328
    - results, 328
    - salt water, 329
    - South Kalgurli, 329
  - Grain, 131
  - Gram-atom, 9
  - Granby Consolidated, fine grinding, 138
  - Graphical presentation, 528
    - arithmetic scale, 529
    - logarithmic scale, 529
  - Graphite, 122, 347
    - Canadian results, 348
    - concentrate screening and tabling, 348-350
    - flakiness, 347
    - gneiss concentration, 347
    - regrinding, 348, 349
  - Gravity concentration *vs.* flotation, 481
  - Grinding, 122, 132, 330, 422, 503
    - arrangement, 422
    - circulating load, 139
    - ideal flow-sheet, 137
    - modern trends, 137
    - optimum conditions, 487
    - practice, 133
    - Sullivan, 135
    - Utah Copper, 138
  - Gum arabic, 363
- H
- Hematite flotation, 375
  - Heptylic acid, 70, 361, 378
  - Herodotus, on flotation, 2
  - Hydrazine, 164
  - Hydroelectrolysis, 532
  - Hydrogen electrode, 509
  - Hydrogen-ion concentration, 29
    - determination of, 507
      - colorimetric, 510
      - electrometric, 509

Hydrogen-ion concentration, determination of, electrometric, *vs.* colorimetric, 511

Roulette comparator, 511

Kydometallurgy, changes in, 531  
*vs.* ore dressing, 531

Hydrosulfides, organic, 72

oxidation products, 73

## I

Ikuno Concentrator, Japan, 268

flow-sheet, 269

reagents, 270

results, 270

Impounding tailing (*see* Tailing impounding)

Independence mill, 332

flow-sheet, 333

Inhibitors, organic, 75

Inspiration, reagent addition, 192

Insurance, 437

Interest on investment, 434

Interface, 15

Ion, 11

hydration, 28

Ionization, mechanism of, 28

Iron, flotation at Midvale, 239

-lead (*see* Lead-iron)

-zinc (*see* Zinc-iron)

## J

Jamesonite, 197

Jarosites, 300

## K

Kansoria plant, 225

reagents, 225

Kaolinization, 129

Katanga, oxidized copper, 307

Kennecott mill, 311

Kerosene, 354, 356

## L

Lake Superior practice, 193

Launder, 405

slopes, 405

Leaching-flotation schemes, 314

Lead-copper ores (*see* Copper-lead ores)

reagent consumption, 220

Lead, custom plants, 475

-iron separation, 212

selectivity indices, 211

nitrate, 382

ores, copper-bearing, 276

reagent consumption, 219

-silver custom plants, 476

smelter schedule, 458, 461

value in concentrate, 463

-zinc ores, 196

Australian practice, 246

copper problem, 216, 218

cyanide, 210

dichromate, 210

effect of micaceous gangue, 209

galena from marmitite, 210

laboratory separation, 212

minerals in, 197

plant design, 430, 431

practice, 223

problems in treatment, 208

reagent consumption, 222, 223

selectivity indices, 211

separation of sulfides from non-sulfides, 209

silver problem, 216, 218

sodium sulfide, 210

sodium sulfite, 210

tonnage treated, 197

zinc recovery, 485, 486

zinc salts, 210

Liberation, 120, 131

definition, 1

degree of, 139

steps in determining, 140

economic limit, 141

percentage, 131

Lime, 161, 170, 181

chalcopyrite, 167

consumption at Britannia, 191

Location of plant, 413

flat site, 414

partly sloping site, 414

sloping site, 414

Losses, 522

Luster, 38

## M

- Machines, pneumatic vs. agitation,**  
115  
(*See also* Flotation machines.)
- Magma Copper ore, 126**
- Magna concentrator, 156**
- Magnetite-apatite, separation, 372**
- Magnetite, flotation, 375**  
-quartz separation, 375
- Malachite, activation, 311, 313**  
-calcite separation, 310  
aromatic hydrosulfides, 312  
lead nitrate, 313  
mercaptans, 311  
xanthates, 310  
-cerussite separation, 316  
-smithsonite separation, 317,  
318  
fatty acids, 306  
mercaptans, 309  
soaps, 306, 307  
sulfidizing, 307, 308  
thiophenols, 309  
xanthates, 308
- Manganese oxide flotation, 375**
- Marmatite, 213**  
-chalcopyrite ores (*see* Chalco-  
pyrite-marmatite ores)  
-pyrite separation, 214  
-pyrrhotite separation, 214
- Mercaptans, 72, 73, 163, 169, 309,  
311**  
amyl, 208, 315  
heptyl, 315, 316
- Mercury, ores, 339**  
-vapor lamps, 426
- Metal markets, effect of flotation,  
533**
- Metallurgical calculations, 522**  
efficiency, 525  
results, direct statement, 522
- Methyl quinoline, 37**
- Miami, flow-sheet, 185**  
mill, 185  
ore, 176, 185  
regrinding, 185
- Miami, results, 187**
- Microscope, 494**  
sizing, 505
- Middling, 132**  
particles, flotation of, 141  
regrinding of (*see* Regrinding)  
returns, 491, 492
- Midvale plant, 238**  
flow-sheet, 240, 241  
general view, 427  
iron flotation, 239  
economics, 239  
minerals, 240  
reagents, 242
- Mill, arrangement, 421**  
building, 439  
design, 411
- Mineral, 120**  
intergrowth, Morning mill, 226  
Sullivan mill, 234
- Mineralization, primary, 125**
- Mineralogical analysis, 498**  
effect of particle size, 501  
of specific gravity, 501  
and flotation results, 499-501  
sampling, 502  
systematic errors, 502
- Mining effect of flotation, 532**
- Missouri lead plant, 224**  
flow-sheet, 224  
reagents, 225  
results, 225
- Mol, 9**
- Molecules, 9**  
speed of orientation, 17
- Molybdenite, 122**  
concentrates, market require-  
ments, 339  
ores, 339
- Monoxanthogen, 72**
- Morning mill, 225**  
flow-sheet, 227  
mineral intergrowth, 226  
particle size, 143-145  
reagents, 229  
regrind circuit, 227  
results, 196

## N

- Native, copper, 169
  - amygdaloid, 193
  - conglomerate, 193
  - pH, 194
  - gold, 324
  - pH, 324
- Nickel-copper ores (*see* Copper-nickel ores)
- Nickel, occurrence, 286
- Non-metallic minerals, 343
  - fatty acids, 358
  - non-polar, 343
  - polar, 358
  - soaps, 358
- Nonylic acid, 70

## O

- Obsolescence, 435
- Octet theory, 10
- Oil, amount, in early processes, 3, 4
  - collecting, 63, 242, 288
  - disuse of, 5
  - pine-tar, 347
  - sulfurized, 294
- Oleic acid, 69, 368
- Operating costs, 444
  - actual, 445, 446
  - balls, 452
  - control, 446
  - distribution, 453
  - labor, 446, 448
    - actual requirements, 446, 449
    - type required, 448
  - power, 450, 451
    - actual requirements, 450
    - distribution, 451
    - at Phelps Dodge mills, 452
  - reagents, 453
  - sources, 446
  - superintendence, 446
  - supplies, 452
  - vs.* tonnage, 446
- Ore, 120
  - dressing, 1
    - changes in, 531
    - vs.* hydrometallurgy, 531

## Ore, genesis, 124

- effect of hydrothermal alteration, 129
- oxidized, 124
- reserves, effect of flotation on, 533
- structure, 124
- sulfide, 124
- texture, 130
- treatment choice, 457
- United Verde, 125
- Organic sulfides or disulfides, 67
- Overgrinding, 132
- Oxidation, 35
- Oxidized, copper minerals, 290
  - copper ores, 305
    - leaching-flotation schemes, 314
    - metallization, 312
  - lead-copper ores, 315
  - lead minerals, 290, 291
  - lead ores, 292
    - conditioning, 301
    - fatty acids, 295
    - organic sulfhydrates, 296
    - practice, 300
    - reagents in practice, 301
    - results in practice, 301
    - soaps, 295
    - sulfidizing, 292, 293
    - sulfidizing agents, 294
    - sulfurized oils, 294
    - tabling, 305
    - typical mill, 304
    - xanthates, 299
- ores, 130, 290
  - clayey gangue, 292
  - gangue, 291
  - lead-silver, 292
  - precious metals, 291
  - selective flotation, 315
  - zinc minerals, 291
  - zinc ores, 313
- Oxidizing agents, chalcopyrite, 167

## P

- Palmitic acid, 70, 307
- Particle, 131
  - free, 131
  - at liquid surface, 152

- Particle, locked, 132
  - maximum size supported by surface tension, 153
  - middling, 132, 141
  - non-polar, 148
    - and Brownian movement, 151
    - very fine, 148-150
  - polar, 147
  - size, 120, 143, 149, 150
  - time sequence, 151
- Patent, Bradford, 5
  - Callow, 3
  - Cattermole, 355
  - DeBavay, 3
  - Delprat, 2, 5
  - Elmore, 3
  - Everson, 2, 5
  - Froment, 3
  - Greenway, Sulman & Higgins, 4
  - Haynes, 2, 7
  - Hellstrand, 6, 207
  - Hoover, 3
  - Keller, 5
  - Lowry and Greenway, 6
  - Macquisten, 3
  - Nibelius, 3
  - Pallanch, 6
  - Perkins, 5
  - Price, 352
  - royalties, 437
  - Schwarz, 5, 292
  - Sheridan and Griswold, 6
  - Sulman, Picard & Ballot, 3
  - Wood, 3
- Pelargonic acid, 70
- Periodic table, 11, 12
- pH, 163, 205, 208
  - scale, 29
  - regulating agents, 55, 78
  - (See also Hydrogen ion.)
- Phase, in flotation, 24
  - gaseous, 24
  - solid, 31
  - in reactions, 34, 35
- Phenol, 62
  - surface tension, 60
- Phenolphthalein, 184
- Phosphate, concentration, 369
  - deposits, 369, 370
- Pilot, plant, 176, 258, 490, 493
  - Flin Flon, 261, 264
  - Sherritt-Gordon, 258
  - tables, 426
  - vanning, 426
- Pine oil, 62
- Plant division, 440
  - cost, concentrate disposal, 443
  - flotation, 440, 442
- Platinum ores, 337
- Plumbojarosite, structural formula, 300
  - xanthates, 299
- Polarity, 13
  - and floatability, 32
  - of minerals, 31
- Polished sections, preparation, 495
- Polishing, equipment, 494
  - powders, 495
- Potter-Delprat process, 86
- Precious metal ores, 291, 320
  - combination treatment schemes, 480
- Primary slime flotation, Anaconda, 183
  - Britannia, 187
- Pulp, 86
  - conductivity, 512
  - determination, 513
  - consistency, 117
  - conveyors, 405
  - dilution, 45, 117, 118
  - dispersed, 44
  - distributors, 402
- Pumps, 405, 426
  - Wilfley sand, 405
- Pyrite, 161
  - arsenopyrite separation, 336
  - Britannia, 189
  - cassiterite separation, 377
  - cupriferous, 157
  - cyanide, 161
  - higher xanthates, 161
  - iron xanthate, 66
  - lime, 161
  - marmatite separation, 214
  - pH, 163
  - prolonged aeration, 162
  - sodium carbonate, 161

Pyrite, sodium sulfide, 163  
 -sphalerite separation, laboratory  
   data, 214  
   sulfuric acid, 163  
 Pyrolusite flotation, 376  
 Pyrometallurgy, changes, 531  
 Pyroxene-garnet, 384  
 Pyrrhotite, Sullivan ore, 234

## Q

Quartz, 361  
   activation, 361, 362  
   inhibition, 362  
   pH, 362

## R

Rare metals, 320  
 Ratio of concentration, 523  
   calculation, 524  
   usefulness and limitations, 524  
 Reagents, 54  
   (See also under specific name.)  
   activating, 55, 75  
   addition *vs.* pH, 508  
   alkaline circuits, 6  
   Anaconda, 184  
   antitoxic, 55  
   Britannia, 190  
   C-C mixture, 303  
   Chief consolidated, 303  
   classification, 54  
   cleansing, 55  
   coal flotation, 352  
   collecting, 55, 63, 64  
   consumption, 82, 83  
     zinc flotation, 211  
   Copper Cliff, 288  
   copper-zinc separation, 252, 255  
   deactivating, 55  
   depressing, 55  
   dispersing, 49, 55  
   feeders, 402  
     apron-conveyor type, 403  
     belt-conveyor type, 403  
     cup-and-wheel type, 404  
     Geary, 404  
     for liquids, 403

Reagents, feeders, for solids, 408  
   for viscous solutions, 405  
   Flin Flin, 264, 265  
   frothing, 54, 62  
   functions, 80  
   Ikuno, 270  
   inorganic, 5  
   Kansoria, 225  
   introduction, 83, 516  
   mixing tanks, 426  
   Morning, 229  
   native copper, 194  
   oxidized ores, 301  
   pH regulation, 55  
   place of addition, 81, 190  
   promoting, 55  
   protective colloids, 55  
   quantity, 81  
   Roan Antelope, 177  
   San Diego, 305  
   Sherritt-Gordon, 260  
   solutions, for testing, 516  
   sulfidizing, 76  
   sulfur flotation, 345  
   Sullivan, 234, 237, 238  
   Timber Butte, 232  
   Tul-mi-chung, 326  
   Tooole, 245  
   use, 81  
   Utah-Apex, 283  
   Utah Copper, 180  
 Recent trends, 6  
 Reclamation of water (*see* Water  
   reclamation).  
 Recovery, 522, 528  
   calculation, 523  
   *vs.* grade of concentrate, 461, 470  
   usefulness and limitations, 524  
 Regrinding, Britannia, 188  
   Miami, 185  
   Morning, 228  
   Sullivan, 236  
 Reinders' equation, 33  
 Rejection, 522  
   usefulness and limitations, 524  
 Rhodochrosite, concentration, 364  
   pH, 364, 365  
   proposed flow-sheet, 366  
   quartz separation, 364



- Rhodochrosite, sodium silicate, 368**  
**Roan Antelope, ore, 157, 176**  
 \* **plant, 177**  
     **reagents, 177**  
     **results, 177**  
**Rod mills, 133**  
**Rolls, 133**
- S**
- Sagebrush oil, 63**  
**Salt, 263**  
**Salt water, 329**  
**Samplers, auto-type, 408**  
     **pulp, 408**  
**Sampling, for slide mounting, 502**  
**San Diego mill, 305**  
     **reagents, 305**  
**Scavenger-cell fluctuations, 425**  
**Scavenging, 142, 424**  
**Schedules, 457-459, 462, 474**  
**Scheelite, concentration, 372**  
     **-quartz separation, 373**  
**Screens, 133, 504**  
**Sedimentation, 44**  
**Selective flotation, 6**  
**Selectivity index, 211, 215, 525**  
     **calculation, 525**  
     **relation to other measures, 526**  
     **use, 525**  
**Semi-oxidized ores, 130**  
     **silver, 130**  
**Sequence of flotation, 151**  
**Sericitization, 129**  
**Sherritt-Gordon, flow-sheet, 259**  
     **pilot mill, 258**  
     **reagents, 260**  
     **results, 260**  
**Shut-downs, 422**  
**Silicates, floatability, 380**  
**Silicification, 129**  
**Silver, colloidal iodide, 43**  
     **mineralogical occurrence, 320**  
     **ores, 337**  
**Size of particles, 142, 143**  
     **Anaconda, 143, 146**  
     **Cananea, 143**  
     **vs. floatability, 142**  
     **Morning mill, 143-145**  
     **Size of particles, vs. selection, 147**  
         **ps. sequence of flotation, 151**  
         **Sullivan concentrator, 143**  
         **United Verde, 143, 147**  
         **upper limit, 152, 153**  
     **Sizing, 504**  
     **Skin flotation, 2**  
         **De Bavay, 3**  
         **Macquisten, 3**  
         **Nibelius, 3**  
         **Wood, 3**  
     **Smelter payment vs. gross value of**  
         **concentrate, 465**  
     **Smelter schedules, 457-459**  
         **typical calculation, 459, 462**  
     **Smelting vs. flotation (see Flotation**  
         **vs. direct smelting)**  
     **Smithsonite-calcite separation, 315**  
     **Soap, 42, 69, 295, 306, 307**  
         **collection of activated silicates, 67,**  
             **331, 381**  
         **detergent action, 42**  
     **Soda ash (see Sodium carbonate)**  
     **Sodium carbonate, 79, 161**  
         **hydroxide, 79**  
         **oleate, 363-365, 368, 372**  
         **silicate, 80**  
         **sulfide, 76, 77, 79, 163, 167, 207,**  
             **210**  
         **sulfite, 210**  
     **Sol, 41**  
     **Soluble salts, 415**  
         **common ions, 416, 417**  
         **mine waters, 417**  
         **Nacozari, 418**  
         **ores, 417**  
         **rivers and lakes, 416**  
         **Timber Butte, 230**  
     **Sørensen, pH, 30**  
     **Sphalerite, activation, 205, 207**  
         **amyl mercaptan, 208**  
         **-bornite separation, 271**  
         **-chalcocite-bornite separation, 272**  
         **chalcopyrite-bearing, 123**  
         **collectors for unactivated, 205**  
         **copper salts, 205, 206**  
         **cyanide, 206**  
         **floatability, 204**

- Sphalerite, pH, 205, 208
    - replaced by argentite, 130
    - sodium sulfide, 207
    - sulfites, 207
    - xanthates, 205
    - zinc salts, 206
  - Spinel, 376
  - Stokes' law, 506
  - Storage-bin, capacity, 422
  - Storing arrangement, 421
  - Strakes, 188
  - Structure of ore, and grinding, 122
  - Substances, heteropolar, 14
    - molecular dissolution, 29
    - non-polar, 14
    - polar, 14
  - Sulfide, organic, 164
    - oxidation, mechanism of, 35
  - Sulfidizing, 292, 293, 307, 308
  - Sulfites, 164, 207
  - Sulfur, 344
    - concentrates, refining difficulties, 346
    - dioxide, 207
    - flotation, reagents, 345
      - results, 345
    - marketing, 346
    - quartz separation, 345
  - Sulfuric acid, 79, 163
  - Sullivan plant, 234
    - crushing and grinding, 135
    - flow-sheet, 136, 235, 236
    - iron content, 234
    - particle size, 143, 145, 147
    - reagents, 234, 237, 238
    - regrinding circuit, 236
    - results, 238
  - Surface, alteration, 34
    - nature of, 35
    - other than oxidation, 36
  - liquids, 15
  - reactions, 15
  - solids, 19
  - tension, 15
    - Chainomatic balance, 517
    - cresol solutions, 59
    - depression, 57
    - liquids, 16
    - measurement, 516
  - Surface, tension, metals, 56
    - organic compounds, 57
    - phenol solutions, 60
    - water, 57
  - Surge tank, 424
    - capacity, 424
- T
- Tabling, 305
  - Tailing, definition, 1
    - disposal, 420
    - cost, 444
    - impounding, 420
    - Inspiration method, 420
    - Zeigler method, 420
    - mine filling, 421
  - Tarnishing, 131
  - Taxes, 438
  - Terpineol, 58, 62
  - Testing, arrangement of equipment, 518
    - batch, 488
    - cells, 514
      - Callow, 515
      - Fahrenwald, 515
      - Kraut, 515
      - Janney, 514
      - MacIntosh, 515
      - University of Utah, 514
    - circuits, 488
    - continuous laboratory unit, 490, 493
    - crushing equipment, 503
    - elutriation, 505
    - equipment, 488
    - flotation, circulating loads, 491, 492
      - equipment, 507
      - technique, 515
    - grinding, -classifying circuits, 491
      - equipment, 503
    - hydrogen-ion determinations, 507
    - microscope sizing, 505
    - mill scale, 490
    - ores, 488
    - pilot plant, 490

**Testing, reagents, 488**  
     screening equipment, 504  
     sizing equipment, 504  
     steps, 488  
**Tetrahedrite, 167**  
**Texture of ore, 121**  
     and concentration, 121  
     extreme fineness, 122  
**Thermodynamics, second law, 17**  
**Thickener, cost, 443**  
     Dorr, 407  
     Genter, 407  
     Hardinge, 407  
     Hydrotator, 407  
     requirement, 443  
     to separate circuits, 425  
**Thiocarbanilid, 74, 171, 245**  
**Thiocarbonate, 164**  
**Thiocresol, 295, 297**  
**Thiophenol, 72, 309, 312**  
**Thiosulfate, 164**  
**Thiourea, 74, 164**  
**Timber Butte mill, 229**  
     flow-sheet, 230, 231  
     minerals, 232  
     reagents, 232  
     results, 233  
     soluble salts, 230  
**Tin ore flotation, 377**  
**Toluidine, 58**  
**Tooele mill, 243**  
     flow-sheet, 244  
     reagents, 245  
     results, 245  
**Toxic agents, 79**  
**Traube's rule, 61**  
**Trent process, 355**  
     comparison with flotation, 357,  
         358  
     performance, 356  
     principle, 355  
**T-T mixture, 171, 172, 192**  
**Tul-mi-chung mill, 324**  
     flow-sheet, 325  
     reagents, 326  
     results, 326  
**Tungstate concentration, 372**

## U

**Undecylic acid, 70**  
**United Verde ore, 125, 162**  
     particle size, 143, 146  
**Utah-Apex mill, 281**  
     flow-sheet, 282  
     reagents, 283  
     results, 283  
**Utah Copper, fine grinding, 138**  
     flow-sheet, 180  
     ore, 128, 129, 176, 178, 179  
     particle size, 169  
     plant, 178, 180  
     reagents, 180  
     recovery, 156  
     results, 181  
     view of mill, 156

## V

**Valence, cohesive, 14**  
     on flocculation, 51, 52  
     residual, 14  
**Valeric acid, 14**

## W

**Water, correction, 418**  
     dissociation, 26-28  
     dissolved impurities, 415  
     flow-lines, 91  
     -gas, tar, 237  
     heating, 420  
     impurities in tailing, 419  
     molecular association, 27  
     Pennycuik, 27  
     polar character, 27  
     quality required, 415  
     quantity required, 415  
     reclaimed, 419  
         salts in, 419  
     reclamation, 415, 419, 420  
     softening, 415  
     storage, 419  
     structure of, 26  
     surface tension, 57  
     variations in, quality, 418  
**Wilfley pump, 405**

Wolframite concentration, 372  
Wright-Hargreaves ore, 331

## X

Xanthates, 70, 169, 199, 204, 205,  
229, 308, 310  
amyl, 113, 267, 334, 335, 337  
vs. ethyl, 299  
coating on azurite, 65  
collection of, galena, 66  
pyrite, 66  
sphalerite, 66  
sulfides, 65  
ethyl, 184, 186, 192  
vs. amyl mercaptan, 208  
higher, 161

Xanthates, octyl, 315  
oxidation products, 72  
preparation, 70, 71  
structural formula, 71  
Xylenol, 58, 62

## Z

Zinc-copper (*see* Copper-zinc)  
-iron separation, 213  
desirability, 213  
selectivity indices, 215  
-lead (*see* Lead-zinc)  
ores, reagent consumption, 221  
refinery schedule, 459, 463  
value in concentrate, 464  
effect of freight rates, 464

